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THE METHOD OF DIFFERENTIALS IN PROBLEMS OF MAXIMA AND MINIMA

By

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1. It is proposed to illustrate the ease and convenience of the method of differentials by solving a few problems in maxima and minima.

The Method of Differentials.—We need note the following points :—

(*i*) The number of *dependent* variables in any problem is equal to the number of relations given. Any of the variables may be chosen as the dependent ones. The remaining (whatever their number) will then be the *independent* variables.

(*ii*) If x is any one of the independent variables, its (first order) differential dx is the same as its arbitrary increment Δx and all its higher order differentials are zero ; that is

$$d^2x = d^3x = d^4x = \ldots = o.$$

(*iii*) If y is any one of the dependent variables then its differentials dy, d^2y, d^3y, $\ldots$ do not in general vanish ; and these can be expressed in terms of the (first order) differentials of the independent variables. Further, $d^r y$ will be a homogeneous function of degree r, in the differentials of the independent variables.

Stationary points : maxima and minima.—Let $u = \phi(x_1, x_2, x_3 \ldots x_n)$ and let it be required to find the stationary points of u and determine which of them are maxima and which are minima.

The variables $x_1, x_2, x_3 \ldots x_n$, may be all independent or they may be connected by some m $(< n)$ relations such as

$$f_r(x_1, x_2, x_3, \ldots x_n) = o, \qquad r = 1, 2, 3 \ldots m.$$

In the former case the problem is said to be a problem of *free* maxima and minima : in the latter case it is a problem of *conditional* maxima and minima.

By definition u is said to be stationary at a point if for *all* arbitrary, small increments of the independent variables, the increment of u has the same sign.

If Δu be positive for all arbitrary increments of the independent variables, u is said to be minimum ; and if Δu is negative, then u is said to be maximum.

Now by Taylor's theorem we have

$$\Delta u = du + \frac{d^2u}{2!} + \frac{d^3u}{3!} + \frac{d^4u}{4!} + \ldots$$

and hence we have the following criteria :—

A necessary condition for the existence of a stationary value is that

$du = o.$

Further if d^2u is a " positive definite form " in the differentials of the independent variables, then the stationary value is a minimum; and if d^2u is a " negative definite form " then the stationary value is a maximum.

If d^2u be an *indefinite* form, there is no stationary value.

If d^2u be a *semi-definite* form further investigation is necessary.

Note.—A polynomial that is homogenous and of the nth degree in two or more variables is called a *form* or a *quantic*.

A form is said to be *definite* if it is is not zero unless its variables are *all* zero.

A definite form has the same sign for all values of its variables and does not vanish unless these are all zero. The form is called a positive definite form or a negative definite form according as the sign is positive or negative.

A form which preserves the same sign but vanishes even when its variables are not *all* zero is said to be *semi-definite*.

A form which does not preserve the same sign is said to be *indefinite*.

2. Example 1. " The variable z is determined as a function of x and y by the equation

$$x^3 + y^3 + z^3 - 6\,xyz + 3 = o.$$

Find the values of $\partial^2z/\partial x^2$, $\partial^2z/\partial y^2$, $\partial^2z/\partial x\partial y$ when $x = y = z = 1$, and prove that these values of x, y, z, make $2\,xy + z^2$ a minimum."

—(Math. Trip. 1923)

Obviously the method expected here was the one of derivatives. We are adopting the " method of differentials ".

We have $u = 2\,xy + z^2,$ . . . .   (1)

subject to $f = x^3 + y^3 + z^3 - 6\,xyz + 3 = o,$ . .   (2)

We choose u and z as the dependent variables, so that x and y become the independent ones and hence $d^2x = d^2y = o$ . . . .   (3)

Differentiating (2) we get

$\Sigma\,(x^2 - 2\,yz)\,dx = \frac{1}{3}\,df = o$ . . . . . .   (4)

and differentiating this once more and remembering (3) we get

$\Sigma\,(2\,xdx - 2\,ydz - 2\,zdy)\,dx + (z^2 - 2\,xy)\,d^2z = o$ . . . . . .   (5)

Now the values $x = y = z = 1$,

reduce (4) and (5) respectively to $dx + dy + dz = o$ . . . .   (6)

and $d^2z = 2\,\Sigma\,dx^2 - 4\,\Sigma\,dydz$ . .   (7)

Consider now du and d^2u :—

$$du = 2\ (ydx + xdy + zdz) \qquad \qquad .. \quad (8)$$

and $d^2u = 2\ (dydx + dxdy + dz^2 + zd^2z)$

$$= 4\ dxdy + 2\ dz^2 + 2\ zd^2z \qquad \qquad .. \quad (9)$$

Now the values $x = y = z = 1$ reduce (8) to

$$du = 2\ (dx + dy + dz)$$

$= 0$, in virtue of (6).

And (9) becomes

$$d^2u = 4\ dxdy + 2\ dz^2 + 2\ d^2z \qquad \qquad .. \quad (10)$$

Substituting for d^2z from (7) we have

$$\tfrac{1}{2}d^2u = 2\ dx^2 + 2\ dy^2 + 3\ dz^2 - 2\ dxdy - 4\ dydz - 4\ dzdx \qquad .. \quad (11)$$

But from (6)

$$0 = (dx + dy + dz)^2 \qquad \qquad .. \quad (12)$$

$$\therefore\ \tfrac{1}{2}d^2u = 3\ dx^2 + 3\ dy^2 + 4\ dz^2 - 2dydz - 2dzdx$$

$$= (dx - dz)^2 + (dy - dz)^2 + 2\ (dx^2 + dy^2 + dz^2)$$

i.e. $d^2u > 0$, unless each differential vanishes.

i.e. d^2u is a positive definite form.

Thus for $x = y = z = 1$ we see that u is a minimum.

3. Example 2. "Having given that $x + y + z = 1$, prove that the expression

$$x^3 + y^3 + z^3 + 6\ nxyz$$

is a maximum when $x = y = z = \tfrac{1}{3}$, if n is greater than unity ; a minimum if n is less than unity ; but neither the one nor the other if n is equal to unity." (St. John's College : June 1888).

We have here

$$u = x^3 + y^3 + z^3 + 6\ nxyz \qquad \qquad .. \quad (1)$$

subject to $f \equiv x + y + z - 1 = 0 \qquad \qquad .. \quad (2)$

We choose u and z as the dependent variables so that x and y become the independent ones and therefore

$$d^2x = d^2y = 0 \qquad \qquad .. \quad (3)$$

Differentiating (2) we get

$$dx + dy + dz = 0 \qquad \qquad .. \quad (4)$$

and further differentiating

$d^2x + d^2y + d^2z = 0$, which in virtue of (3) reduces to

$$d^2z = 0 \qquad \qquad .. \quad (5)$$

Consider now du and d^2u :—

$$du=\Sigma(3\,x^2+6\,nyz)\,dx \qquad \qquad .. \quad (6)$$

and $d^2u=\Sigma(6x\,dx+6\,nydz+6\,nzdy)\,dx.$ $\qquad .. \quad (7)$

But the values $x=y=z=\frac{1}{3}$ reduce (6) and (7) respectively to

$du=0$, in virtue of (4)

and $d^2u=2\,\Sigma(dx+ndz+ndy)\,dx$

$\qquad =2\,\Sigma\,dx^2+4n\,\Sigma\,dydz$

$\qquad \therefore \frac{1}{2}d^2u=(1-n)\,\Sigma dx^2$, using $\Sigma dx=0$.

Thus we see that d^2u is a positive definite form if $n<1$, and we have a minimum; if $n>1$, d^2u is a negative definite form giving a maximum.

If $n=1$, $d^2u=0$, the form is *semi-definite* and we have to investigate further.

Differentiating (7) and remembering that $d^2x=d^2y=d^2z=0$ we get,

$d^3u=\Sigma\,(6dx^2+6\,n\,dydz+6\,n\,dzdy)\,dx$

i.e. $\frac{1}{6}\,d^3u=\Sigma\,dx^3+6\,dxdydz,\,(n=1)$.

This shows that $d^3u\neq o$ and hence $\triangle u$ cannot preserve the same sign and there is no maximum nor minimum for u in this case.

4. Example 3. " If x, y, z are connected by $x^2+y^2+z^2=a^2+b^2+c^2$, $(abc\neq0)$ shew that the following conditions are sufficient for $f(x)+g(y)+h(z)$ to have a maximum at $(a,\,b,\,c)$:—

$$\frac{f'(a)}{a}=\frac{g'(b)}{b}=\frac{h'(c)}{c}$$

and $\qquad \qquad (A+B)<0<AB+BC+CA,$

where $A=\dfrac{f''(a)}{a^2}-\dfrac{f'(a)}{a^3}$

$B=\dfrac{g''(b)}{b^2}-\dfrac{g'(b)}{b^3}$

$C=\dfrac{h''(c)}{c^2}-\dfrac{h'(c)}{c^3}$. "

—(Math. Trip. II 1929)

We have here

$$u\equiv f(x)+g(y)+h(z) \qquad .. \qquad .. \qquad .. \quad (1)$$

subject to $\phi=(x^2+y^2+z^2)-(a^2+b^2-c^2)=o \qquad .. \quad (2)$

Choose u and z as the dependent variables so that x and y become the independent ones and therefore $d^2x=d^2y=o$ $\qquad .. \quad (3)$

From (2) we get

$$x \, dx + y \, dy + z \, dz = o \qquad \qquad .. \quad (4)$$

and further in virtue of (3)

$$d \, x^2 + d \, y^2 + d \, z^2 + z \, d^2z = o \qquad \qquad .. \quad (5)$$

At (a, b, c) these relations (4) and (5) become

$$a \, dx + b \, dy + c \, dz = o \qquad \qquad .. \quad (6)$$

and
$$dx^2 + dy^2 + dz^2 + cd^2z = o \qquad \qquad .. \quad (7)$$

Consider now du and d^2u :—

$$du = f'(x) \, dx + g'(y) \, dy + h'(z)dz \qquad \qquad .. \quad (8)$$

$$d^2u = f''(x) \, dx^2 + g''(y) \, dy^2 + h''(z)dz^2 + h'(z) \, d^2z \qquad .. \quad (9)$$

In virtue of (6), $du = o$ at (a, b, c) if $\dfrac{f'(a)}{a} = \dfrac{g'(b)}{b} = \dfrac{h'(c)}{c}$ (10)

Further, eliminate d^2z between (9) and (7) and we get at (a, b, c) for d^2u

$$\left[f''(a) - \frac{h'(c)}{c} \right] dx^2 + \left[g''(b) - \frac{h'(c)}{c} \right] dy^2 + \left[h''(c) - \frac{h'(c)}{c} \right] dz^2$$

i.e., in virtue of 10

$$d^2u = Aa^2 \, dx^2 + Bb^2 \, dy^2 + Cc^2 \, dz^2 \qquad \qquad .. \quad (11)$$

Substituting for dz from (6) we get d^2u equal to

$$(A + C) \, a^2dx^2 + 2ab \, C \, dxdy + (B + C) \, dy^2$$

Obviously this is a definite form if the roots are imaginary,

i.e., if $\qquad \qquad o < AB + BC + CA$

Further, for maximum $A + C < o$

In fact then $B + C < o$ and similarly $A + B < o$

Thus, the necessary condition for the existence of stationary value is :

$$AB + BC + CA < o$$

And if further A, B, C are negative, we have a maximum and if A, B, C are positive we have a minimum.

5. Example 4. " If x, y, z be three variables connected by a symmetrical equation $\phi(x, y, z) = o$, of which $x = y = z = a$, is a solution, shew that another symmetrical function $f(x, y, z)$ has maximum or minimum value at (a, a, a) according as

$$\phi_x{}^2 \, (f_{xy} - f_{xx}) + \phi_x \, f_x \, (\phi_{xx} - \phi_{xy})$$

is positive or negative at (a, a, a) "

—(Bombay Univ. M.A. 1930)

Here we have

$$u = f(x, y, z) \qquad \qquad .. \quad (1)$$

subject to

$$\phi(x, y, z) = o \qquad \qquad .. \quad (2)$$

Choose u and z as dependent variables, so that x and y are independent and hence

$$d^2x = d^2y = o \qquad \qquad .. \quad (3)$$

From (2) we get

$$\phi_x dx + \phi_y dy + \phi_z dz = o \qquad \qquad .. \quad (4)$$

and using (3) we have from this

$$o = d^2\phi = \phi_{xx}dx^2 + \phi_{yy}dy^2 + \phi_{zz}dz^2$$
$$+ 2\phi_{xy}dxdy + 2\phi_{yz}dydz + 2\phi_{zx}dzdx$$
$$+ \phi_z d^2z \qquad \qquad .. \quad (5)$$

Similarly

$$du = f_x dx + f_y dy + f_z dz \qquad \qquad .. \quad (6)$$

and

$$d^2u = f_{xx}dx^2 + f_{yy}dy^2 + f_{zz}dz^2$$
$$+ 2f_{xy}dxdy + 2f_{yx}dydz + 2f_{zx}dzdx$$
$$+ f_z d^2x \qquad \qquad .. \quad (7)$$

Now since f and ϕ are symmetrical functions in x, y, z, therefore for $x = y = z = a$ we must have

$$
\left.
\begin{aligned}
f_x = f_y = f_z \qquad \text{and} \qquad \phi_x = \phi_y = \phi_z \\
f_{xx} = f_{yy} = f_{zz} \qquad\qquad \phi_{xx} = \phi_{yy} = \phi_{zz} \\
f_{xy} = f_{yz} = f_{zx} \qquad\qquad \phi_{xy} = \phi_{yz} = \phi_{zx}
\end{aligned}
\right\} \quad .. \quad (8)
$$

Now in virtue of (4) and (8) we get from (6)

$$du = o \qquad \qquad .. \quad (9)$$

Again, in virtue of (8), (5) and (7) reduce respectively to

$$o = d^2\phi = \phi_{xx}\Sigma dx^2 + 2\phi_{xy}\Sigma dydz + \phi_x d^2z \qquad \qquad .. \quad (10)$$

and

$$d^2u = f_{xx}\Sigma dx^2 + 2f_{xy}\Sigma dydz + f_x d^2z \qquad \qquad .. \quad (11)$$

Eliminating d^2z we have

$$d^2u = \left[f_{xx} - \phi_{xx}\frac{f}{\phi_x} \right]\Sigma dx^2 + 2\left[f_{xy} - \phi_{xy}\frac{f_x}{\phi_x} \right]\Sigma dydz$$

$$= \lambda\Sigma dx^2 + 2\mu\Sigma dydz, \text{ say}$$

$$= (\lambda - \mu)\,\Sigma dx^2 \qquad \qquad \because \ \Sigma dx = o, \text{ from (4)}$$

Thus obviously u is a maximum or minimum according as $(\mu-\lambda)$ is positive or negative, which reduces to the given condition after multiplication by a positive factor $\phi_x{}^2$.

6. Example 5. The variables x, y, z satisfy the equation

$$\phi(x) \, . \, \phi(y) \, . \, \phi(z) = d^3 \, ;$$

shew that if $\phi(a) = d \neq o$ and $\phi'(a) \neq o$, the expression $f(x)+f(y)+f(z)$ is a maximum when $x=y=z=a$ provided that

$$f'(a) \left\{ \frac{\phi''(a)}{\phi'(a)} - \frac{\phi'(a)}{\phi(a)} \right\} > f''(a)$$

We have here

$$u = f(x)+f(y)+f(z) \qquad \qquad .. \quad (1)$$

subject to

$$\phi(x) \, . \, \phi(y) \, . \, \phi(z) - d^3 = o \qquad \qquad .. \quad (2)$$

Choose u and z as dependent variables so that x, y, become independent and hence

$$d^2x = d^2y = o \qquad \qquad .. \quad (3)$$

From (2) we get

$$\frac{\phi'(x)}{\phi(x)} \, dx + \frac{\phi'(y)}{\phi(y)} \, dy + \frac{\phi'(z)}{\phi(z)} dz = o \qquad \qquad .. \quad (4)$$

and differentiating this and using (3)

$$\Sigma \, \frac{\phi''(x) \, . \, \phi(x) - \phi'^2(x)}{\phi^2(x)} dx^2 + \frac{\phi'(z)}{\phi(z)} \, d^2z = o \qquad \qquad .. \quad (5)$$

At (a, a, a) these relations reduce to

$$dx+dy+dz = o \qquad \qquad .. \quad (6)$$

and

$$\frac{\phi''(a) \, \phi(a) - \phi'^2(a)}{\phi^2(a)} \Sigma \, dx^2 + \frac{\phi'(a)}{\phi(a)} \, d^2z = o \qquad .. \quad (7)$$

Consider now du and d^2u :—

$$du = f'(x) \, dx + f'(y) \, dy + f'(z)dz$$
$$= f'(a) \, \Sigma \, dx \qquad , \text{ at } (a, a, a)$$
$$= o \qquad , \text{ in virtue of (6)}$$

And $d^2u = f''(x) \, dx^2 + f''(y) \, dy^2 + f''(z)dz^2 + f'(z) \, d^2z$

$$= f''(a) \, \Sigma \, dx^2 + f'(a) \, d^2z \qquad \qquad .. \quad (8)$$

Eliminating d^2z between (7) and (8) we get

$$d^2u = \left[f''(a) - \frac{f'(a)}{\phi(a) \, . \, \phi'(a)} \left\{ \phi''(a) \, \phi(a) - \phi'^2(a) \right\} \right] \Sigma \, dx^2 \, .. \quad (9)$$

Now if u is to be a maximum the expression in the rectangular brackets

must be negative, i.e., $f'(a) \left\{ \dfrac{\phi''(a)}{\phi'(a)} - \dfrac{\phi'(a)}{\phi(a)} \right\} > f''(a).$

7. Remarks. The reader will note that the principal point is to determine whether d^2u is or is not a definite form. The following cases are worth noting :—

(i) If the quadratic for d^2u breaks into two linear factors, then d^2u cannot be a definite form.

(ii) If the differential of some independent variable be explicitly absent from the quadratic expression for d^2u, then it cannot be a definite form.

(iii) In a case like the following when $u = (y+z)^2 + (z+x)^2 + xyz$, we have $du = o$ at (o, o, o) and $d^2u = 2(dy+dz) + 2(dz+dx)^2$

Now d^2u vanishes, when $dx = dy = - dz$

Thus d^2u preserves the same sign but vanishes even when its variables are not *all* zero. Hence the form is semi-definite and further investigation becomes necessary.

(iv) In Peano's example, quoted by Gibson (page 413), we have

$$u - 8x^2 - 6xy^2 + y^4$$

At (o, o) we get $d^2u = 16\,dx^2$. This preserves the same sign but vanishes when $dx = o$, whatever dy may be. Hence the form is *semi-definite* and for that reason further investigation becomes necessary.

A NOTE ON RIEMANN INTEGRATION

By

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1. It is proposed to establish *ab initio* the result

$$\int_a^b x^m \, dx = \frac{b^{m+1} - a^{m+1}}{m+1}.$$

The method uses only one simple result in algebra, viz.

$$p^{m+1} - q^{m+1} = (p - q)(p^m + p^{m-1} q + \ldots + p q^{m-1} + q^m).$$

Dividing (a, b) into sub-intervals, as

$$a = x_0 < x_1 < x_2 < \cdots < x_n = b,$$

we have

$$\int_a^b x^m \, dx = \text{the common limit of}$$

$\sum_1^n M_r (x_r - x_{r-1})$ and $\sum_1^n m_r (x_r - x_{r-1})$, where M_r and m_r are the bounds of x^m in (x_{r-1}, x_r). Now x^m being continuous is integrable—so the common limit does exist, the question being to find it.

Obviously if μ_r is any number such that $M_r > \mu_r > m_r$, then

$\sum_1^n \mu_r (x_r - x_{r-1})$ has also the same limit I.

Now, in the interval (x_{r-1}, x_r) the bounds of x^m are x_r^m and x^m_{r-1} and *between* these lie the numbers :—

$$x_r^{m-1} x_{r-1}, \quad x_r^{m-2} x_{r-1}^2, \quad \ldots \ldots, \quad x_r^2 x^{m-2}_{r-1}, \quad x_r x^{m-1}_{r-1}.$$

∴ I = the limit of *any* of the following $(m + 1)$ expressions :—

$$\sum_1^n x_r^m (x_r - x_{r-1})$$

$$\sum_1^n x_r^{m-1} x_{r-1} (x_r - x_{r-1})$$

$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot$$

$$\sum_1^n x_r x^{m-1}_{r-1} (x_r - x_{r-1})$$

and

$$\sum_1^n x^m_{r-1} (x_r - x_{r-1})$$

∴. Adding we get

$(m + 1)\ I = $ limit of the expression

$$\sum_1^n (x_r{}^m + x_r{}^{m-1}\, x_{r-1} \ldots + x^m{}_{r-1})\,(x_r - x_{r-1})$$

$$= \lim \sum_1^n (x_r{}^{m+1} - x_{r-1}{}^{m+1})$$

$$= \lim (x_n{}^{m+1} - x_o{}^{m+1})$$

$$= \lim (b^{m+1} - a^{m+1})$$

no need to take the limit now and we get

$$I = \frac{b^{m+1} - a^{m+1}}{m + 1}$$

2. A slightly different device enables us to prove *ab initio* the results

$$\int_a^b \sin x\ dx = \cos a - \cos b\ ;$$

and $\displaystyle\int_a^b \cos x\ dx = \sin b - \sin a.$

With the usual notation we have

$$\int_a^b \sin x\ dx = \lim \sum_1^n \mu_r\,(x_r - x_{r-1})$$

Take $\mu_r = \sin \dfrac{x_r + x_{r-1}}{2}$, and since each $(x_r - x_{r-1}) \to 0$, replace

it by $2 \sin \dfrac{x_r - x_{r-1}}{2}$; so that

$$\int_a^b \sin x\ dx = \lim \sum_1^n 2 \sin \frac{x_r + x_{r-1}}{2}.\ \sin \frac{x_r - x_{r-1}}{2}$$

$$= \lim \sum_1 (\cos x_{r-1} - \cos x_r)$$

$$= \lim (\cos x_o - \cos x_n)$$

$$= \cos a - \cos b$$

Again,

$$\int_a^b \cos x\ dx = \lim \sum_1^n \mu_r\,(x_r - x_{r-1})$$

$$= \lim \sum_1^n 2 \cos \frac{x_r + x_{r-1}}{2}.\ \sin \frac{x_r - x_{r-1}}{2}$$

$$= \lim \sum_1^n (\sin x_r - \sin x_{r-1})$$

$$= \lim (\sin x_n - \sin x_o)$$

$$= \sin b - \sin a$$

3. To prove that $\int_a^b \sec^2 x \, dx = \tan b - \tan a$.

$$I = \lim \sum_1^n \mu_r \, (x_r - x_{r-1})$$

Put $\mu_r = \sec x_r . \sec x_{r-1}$

and replace $(x_r - x_{r-1})$ by $\sin (x_r - x_{r-1})$; we get

$$I = \lim \sum_1^n \frac{\sin (x_r - x_{r-1})}{\cos x_r . \cos x_{r-1}} = \lim \sum_1^n (\tan x_r - \tan x_{r-1})$$

$$= \tan b - \tan a$$

In exactly the same way we get

$$\int_a^b \operatorname{cosec}^2 x \, dx = \cot a - \cot b.$$

4. Lastly we shall show how we can demonstrate

$$\int_a^b \frac{1}{x} \, dx = \log \frac{b}{a}.$$

$$I = \lim \sum_1^n \mu_r \, (x_r - x_{r-1})$$

Since a unique limit exists $\left(\frac{1}{x} \text{ being integrable} \right)$ it is immaterial in what mode we calculate it. So

put $x_r = ak^r$, $x_{r-1} = ak^{r-1}$, etc.

and choose $u_r = 1/ak^{r-1}$. We get

$$I = \lim \sum_1^n \frac{1}{ak^{r-1}} (ak^r - ak^{r-1})$$

$$= \lim \sum^n (k-1)$$

$$= \lim n \, (k-1)$$

But $\quad b = x_n = ak^n$

i.e., $k = (b/a)^{1/n}$

$$\therefore \; I = \lim n \left[\left(\frac{b}{a} \right)^{1/n} - 1 \right], \qquad \text{as } n \to \infty,$$

$$= \log \frac{b}{a}.$$

STUDIES IN EDUCATIONAL STATISTICS, III*

(Comparative Examination Efficiency of Colleges Affiliated to the University of Bombay in respect of I.A., I.Sc. Examinations 1919-38 and B.A., B.Sc. Examinations 1921-40)

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IN the second paper of this series of educational statistics (See Fergusson College Magazine, February 1941 issue, pp. 4-13), the results of colleges were analysed and the colleges were ranked on the strength of the results of the First Year (F.Y.) Examination and the Second Year (S.Y.) Examinations. In this paper the two S.Y. Examinations are considered separately as they are held : (i) Intermediate Examination in Arts (I.A.) and (ii) Intermediate Examination in Science (I.Sc.). In addition the B.A. (Bachelor of Arts) and B.Sc. (Bachelor of Science) Examinations are taken into account. In this University the B.A. and the B.Sc. Examinations can be taken only after passing the I.A. and I.Sc. Examinations respectively and attending an affiliated college for at least two years.

The efficiency that most colleges (and schools also) in this country care for and put forth an effort to achieve is examination efficiency (i.e., getting as great a percentage of passes as possible) judged by the results of examinations, as at present conducted by the University, for which they prepare candidates. It is, therefore, only this efficiency that I have proceeded to test without examining the merits of the accepted definition of efficiency.

The suggestion is due to Professor D. D. Kosambi (my colleague in the Fergusson College, Poona 4—India) that R. A. Fisher's methods of analysis of variance should be directly applied to these percentages, treating them as plot yields. A difficulty that immediately arises is that the average of the percentages for many years or colleges does not coincide with the true mean, because the numbers appearing from different colleges and for different years are not the same. He further suggests that, as a check, an alternative method may be followed in which the variance is measured from a general " population mean " rather than from the mean of percentages and the number of degrees of freedom is correspondingly increased by a unit. But this does not make any appreciable difference in the result.

Kosambi finally suggests that instead of using the ordinary percentages as plot yields, treat the numbers appeared and passed for each college-

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year as preliminary and experimental plot yields. The number passed should then be adjusted for the number appeared by using Fisher's methods as explained in Ex. 46·1 of Fisher's " Statistical Methods for Research Workers."

In this paper I have dealt with only ordinary percentages. The adjusted numbers will be analysed in a supplementary note.

The best examination efficiency would mean the highest possible average with the least possible variance. The t test is primarily designed to test the significance of means and the z test is to test the significance of variances. In determining the order of merit of colleges, the t test must be applied and not the z test which would only test consistency and not efficiency as we understand it. The following tables, given at the end, are prepared for the purpose :—

Table 1 —I.A. percentages 1916–1940 : all colleges.

Table 2 —B.A. percentages 1916–1940 : all colleges.

Table 3 —I.Sc. percentages 1916–1940 : all colleges.

Table 4 —B.Sc. percentages 1916–1940 : all colleges.

Table 1a—Precis I.A. examination 1919–1938 : selected colleges.

Table 2a—Precis B.A. examination 1921–1940 : selected colleges.

Table 3a—Precis I.Sc. examination 1919–1938 : selected colleges.

Table 4a—Precis B.Sc. examination 1921–1940 : selected colleges.

From these tables the percentages in heavy type only are used for analysis of variance and comparison of efficiency. It will thus be seen that the efficiency of only twelve colleges for the Arts Examinations and only seven colleges for the Science Examinations is considered on the strength of their results for twenty years ; the number of ex-students is taken as if coming from an additional college. It may be seen from the tables that the I.Sc. examination has the smallest mean and may be considered as the stiffest examination. The percentage of the B.Sc. result has distinctly increased after 1930 ; the mean of the first nine years is 59·7 while that of the last eleven years is 76·1. The year 1926 appears to be generally a bad year for all colleges in all examinations.

With the help of the precis tables the colleges may be ranked either by their true means or by their average percentages. But this ranking by means alone cannot indicate in which cases the difference in rank is real and significant and in which cases it is a chance difference.

If the t test is directly applied to the results of colleges when each is to be compared with every other, the process would be very laborious, e.g., for 13 colleges the number of calculations would be 78 ; besides the effect of common examiners, etc., would not be eliminated.

To avoid this and to eliminate the natural effects of examiners, text books and other factors common to colleges for a given period, we resort to the analysis of variance with the help of which we can break up the total sum of squares into its components, viz., (i) due to variation

between colleges, (ii) due to variation between years, and (iii) due to all remaining causes which we may call random variation. The last two components together may be further split up by grouping the twenty years into quinquennia; so that the standard deviation (s.d.) and therefore the critical difference (c.d.) is further reduced. From these component sums of squares we estimate the variance by dividing by the proper number of degrees of freedom and then apply the z test for testing the compatibility. Here are tables (1b, 2b, 3b, 4b, 1c, 2c, 3c, 4c)

Analysis of Variance—Without Grouping Years into Quinquennia

TABLE 1-b

I.A. Examination

	D.F.	S.S.	M S.	F.	S.D.
Colleges	12	12536·27	1044·69	15·94	
Years	19	13294·19	699·69	10·68	
Residual	228	14938·74	65·52	....	8·09
Total	259	40769·20	157·41	2·40	

TABLE 2-b

B.A. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Colleges	12	22603·98	1883·66	28·71	
Years	19	15271·55	803·76	12 25	
Residual	228	14959·79	65·61	....	8·10
Total	259	52835·32	203·99	3·11	

TABLE 3-b

I.Sc. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Colleges	7	4235·41	605·06	7·77	
Years	19	8299·24	436·80	5·61	
Residual	133	10359·17	77·89	....	8·82
Total	159	22893·82	143·99	1·85	

TABLE 4-b

B.Sc. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Colleges ..	7	20596·06	2942·29	24·52	
Years ..	19	12618·82	664·15	5·53	
Residual ..	133	15959·38	119·99	....	10·95
Total ..	159	49174·26	309·27	2·57	

Analysis of Variance—After Grouping Years into Quinquennia

TABLE 1-c

I.A. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Quinquennia ..	3	6805·03	2268·34	37·49	
Colleges ..	12	12536·27	1044·69	17·26	
Q. × C. ..	36	3321·38	92·26	1·52	
Years within 'Q's.	16	6489·16	405·57	6·70	
Residual ..	192	11617·37	60·51	....	7·78
Total ..	259	40769·21	157·41	....	

TABLE 2-c

B.A. Examination

	D F.	S.S.	M.S.	F.	S.D.
Quinquennia .	3	5778·02	1926·01	31·52	
Colleges ..	12	·22603·98	1883·66	30·83	
Q. × C. ..	36	3229·10	89·70	1·47	
Years within 'Q's. ..	16	9493·53	593·34	9·71	
Residual ..	192	11730·69	61·10	....	7·82
Total ..	259	52835·32	203·10	....	

TABLE 3-c

I.Sc. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Quinquennia ..	3	1143·16	381·05	5·39	
Colleges ..	7	4235·41	605·06	8·56	
Q. × C. ..	21	2445·03	116·43	1·65	
Years within 'Q's. ..	16	7156·81	447·25	6·33	
Residual ..	112	7914·14	70·66	....	8·41
Total ..	159	22893·82	143·99	....	

TABLE 4-c

B.Sc. Examination

	D.F.	S.S.	M.S.	F.	S.D.
Quinquennia ..	3	11790·09	3930·03	33·33	
Colleges ..	7	20596·06	2942·29	24·96	
Q. × C. ..	21	2755·18	131·20	1·11	
Years within 'Q's. ..	16	828·73	51·79	0·44	
Residual ..	112	13204·20	117·89	....	10·86
Total .	159	49174·26	309·27	. .	

of the analysis of variance of the examinations considered. The b tables give the analysis without grouping the years into quinquennia and the c tables give it after such grouping. It may be noted that the s.d. is smaller for the arts examinations and the B.Sc. has the largest s.d.

The s.d. obtained from the analysis of variance enables us to calculate the critical difference (c.d.) for $p = ·05$, which quickly tells us whether the difference in the means of two colleges is significantly great. We may then arrange the colleges in groups, the difference between the means of colleges within the same group not being significantly great. Here is a table (Table 5) showing the group to which each college belongs in

TABLE 5

Ranking of Colleges

Colleges	I. A. Examination		B. A. Examination	
	Mean 1919–38	Group and Rank	Mean 1921–40	Group and Rank
Elphinstone ..	70·8	I, 1	81·4	I, 1
Wilson ..	63·3	II, 2	77·5	I, 6
St. Xavier's ..	58·4	III, 4	77·8	I, 5
Gujarat ..	59·6	III, 3	79·4	I, 2
Rajaram ..	45·1	IV, 12	67·5	III 11
Baroda ..	52·1	IV, 10	67·5	III, 11
Fergusson .	55·4	IV, 8	70·9	III, 8
Samaldas ..	58·1	III, 6	79·1	I. 3
D. J. Sind ..	53·9	IV, 9	78·8	I, 4
Bahauddin ..	58·1	III, 5	72·9	II, 7
Sir P. ..	55·9	IV, 7	70·4	III, 9
Karnatak ..	51·0	V, 11	69·3	III, 10
Ex. ..	43·2	VI, 13	44·2	VIII, 13
		C.D. = 4·92		C.D. = 4·94

Colleges	I.Sc. Examination		B.Sc Examination	
	Mean 1919–38	Group and Rank	Mean 1921–40	Group and Rank
Elphinstone ..	63·8	I, 1	79·5	I, 1
Wilson ..	53·3	II, 3	73·7	I, 5
St. Xavier's ..	52·6	III, 4	75·3	I, 3
Gujarat ..	59·7	I, 2	78·6	I, 2
Baroda ..	51·6	III, 5	74·3	I, 4
Fergusson ..	48·0	III, 8	58·9	III, 7
D. J. Sind ..	49·2	III, 7	66·2	II, 6
Ex. ..	49·8	III, 6	43·9	VI, 8
		C.D. = 5·32		C.D. = 6·86

each examination and the general rank of the college in it. The results of colleges in each group can be further tested for quality by the chi-square test in which account is taken also of the numbers securing first and second classes.

There is yet another thing one may like to know in connection with the examination results. This is whether the results of the examinations are correlated, either for the same college or for the University as a whole. It is for this reason that I have considered the results of the I.A. and I.Sc. examinations for 1919-1938 and those of the B.A. and B.Sc. examinations for 1921-1940; so that the result of largely the same batch of students is considered in both the examinations on either side, arts and science. The idea is to find whether a batch of students, which shows a particular result (good, bad or medium) at the earlier examination shows the same type of result in the following examination. On a glance at the precis tables it seems curious that the correlation coefficient (r) for any college or all the colleges together is not significant. But the analysis of covariance will immediately show the true nature of the correlation. Tables of the analysis of covariance are, therefore, calculated (Tables 6 and 7).

Analysis of Covariance

TABLE 6

I.A. (x) against B A. (y)

	D F	Σx^2	Σxy	F_y^2	r	n'	S/n'	Rat o
Colleges	12	12536 27	13180 01	22603 98	+0 78	22	475 99	14·46
Years	19	13294 19	3529 52	15271 55	+0 25	36	383 46	11 66
Residual	228	14938 75	— 803 02	14959 79	—0 05	454	32 88	
Total	259	40769 21	+15906 51	52835 32	0 34	516	84 50	2·57

TABLE 7

I.Sc. (x) against B.Sc. (y)

	D F	Σx^2	Σxy	Σy^2	r	n'	S/n'	Ratio
Colleges	7	4235 41	+ 6248 26	20596·06	+0·67	12	578 50	11 92
Years	19	8299 24	+ 651 02	12618·82	+0 06	36	283·69	5 84
Residual	133	10359 17	+ 1121 97	15959 37	+0·09	264	48·52	.
Total	159	22893 82	+ 8021 25	49174·25	+0 24	316	103·10	2·12

It will be seen from these tables that for examinations on both sides arts and science, there is a positive correlation between colleges eliminating years and also between years eliminating colleges ; but there is a negative correlation for the random component on the arts side only. This is as may be expected ; because the more efficient colleges should pass more students and the annual groups of naturally more intelligent students should pass in greater numbers. If, however, a greater number pass the earlier examination by mere chance the percentage in the next examination should be naturally lower. But looking at the actual results we find that only one correlation is significant between colleges ($n = 18$, $r = \cdot 3783$, for $p = \cdot 1$) and only in Arts. The last three columns of the tables refer to Kosambi's extension of Fisher's z test (See " Current Science, No. 4, of April 1941, pp. 191-193).

n' (new degrees of freedom)$= 2$ (old D.F.$- 1$) ; $S^2 = \Sigma x^2 . \Sigma y^2 - (\Sigma xy)^2$.

S/n' is to be used in place of original mean squares for this extended z test. The last column gives the ratio of $S n'$ in each row against the residual $S n'$. It may be noticed that according to Kosambi's formula the new D.F. are not additive as for a single variate ; because the quantity S cannot be split up into additive components like the sum squares for a single variate. This method enables us to test whether the analysis of covariance is significant with respect to two examinations at a time, regardless of the individual significance of s_x^2, s_y^2 and r. It is clear from the last column that the original generalised variance ($S n'$) of the total has been significantly reduced even at $\cdot 1$ per cent. but the corresponding generalised variances for colleges as well as for years are enormously more significant. To test mean values we should have to apply Hotelling's T^2 in some suitable form. It is to be noted that for both arts and science examinations the ratio of generalised variances for colleges to that for years is practically insignificant at the 5 per cent. level. In other words, the effect of training plus selection is of about the same order as the effect of natural ability plus examiners, etc. What is significant, however, is that the variation due to colleges is greater than that due to years, in each case.

May 24, 1941

TABLE I

I. A. Examination percentages : 1916 to 1940—Bombay University

Year	Elph.	Wil.	St. X.	Guj.	Raj.	Bar.	Fer.	Sam.	D. J.	Bah.	Sir P.	K. C.	Ex.	Uni.
1916	83·6	65·0	62·2	72·8	35·8	55·9	54·4	51·7	65·7	66·7	..	..	39·7	59·9
1917	93·0	70·8	73·6	75·0	46·7	54·0	59·7	67·3	83·0	64·2	51·6	..	45·4	62·3
1918	67·6	52·2	56·6	56·3	69·2	43·9	57·4	61·9	66·1	56·5	54·1	45·9	38·3	52·8
1919	78·3	72·0	55 9	75·6	48 7	67·4	67·4	72·4	80·0	61·7	61·4	51·9	54·5	64·5
1920	84·1	61·4	62·1	59·0	61·5	61·5	71·3	77·8	64·3	55·4	68·8	55·2	46·6	61·6
1921	74·5	66·3	55·0	60 8	37·8	56·1	70·6	42·1	57·8	76 3	63·3	62·1	44·3	57·3
1922	72·1	59·2	59·4	37·7	52·2	48·7	63·0	57·1	56·8	63·3	45 5	38 5	39·9	51·9
1923	84·9	53·8	45·3	54·3	46·4	61·2	68·3	33 3	53·8	58·3	59·4	71·1	42·4	54·0
1924	67·7	69·4	58·7	65·7	27·2	55·3	58·9	70 5	63·6	58 6	65 3	51 9	46·4	56·3
1925	67·5	48·1	40·8	44·7	29·5	40·5	42·2	40 0	51·3	59 4	45·0	35·9	33·9	43·7
1926	62·5	45·7	44·1	36 5	28·6	36·4	42·1	50·0	39·2	56 5	55 2	27·5	37·7	40·0
1927	59·0	47·2	44·3	61·7	40·5	37·0	43·0	44 1	34·9	52·8	38 8	35·9	28·3	39·1
1928	70·8	62·8	52·5	55·1	41·0	50·4	47·7	38 8	37 5	39·0	37·9	47·2	27·7	42·3
1929	68·1	58·3	55·6	32·2	34·0	42·9	37·4	45·9	46 8	53·7	31·4	49 4	30·0	41·1
1930	74·0	56·4	64 2	65·3	39·2	46·5	41 2	51·8	57 6	63·7	43 4	48·9	45·8	50·0
1931	68·0	73·5	70·7	71·8	51·5	50·3	52·5	68·1	43 8	52·1	59 1	47·7	44·3	53·4
1932	78·3	82·2	66·7	65·1	46 7	56·9	61·1	69 0	50·5	51·7	62·0	47·2	58·0	59·4
1933	78·8	72·7	71 9	71·3	45·9	46·0	49·4	77·0	67·2	52·5	70·4	64·6	45·7	58·4
1934	65·7	64·1	56·7	58·5	43·1	73·0	65·7	71·7	58·0	63·3	70·5	73·7	47·6	59·5
1935	68·5	61·5	70·5	74·4	61·8	56·7	59·1	55·2	67·5	59·3	61·0	61·0	50·6	58·6
1936	56·0	60·3	57 1	64 0	49·3	43·4	52·5	64·2	46·4	57 1	56·3	63·5	40·5	50·7
1937	74·8	77·6	64 4	78·1	58·3	53·7	54·3	69·6	47·3	70·7	60 9	48·1	48·9	57·9
1938	63·4	73·0	71·3	59·6	59·4	57·8	61·1	63·5	53·3	57·4	62·8	39·3	50·9	58·9
1939	68·2	79 2	59·7	76·9	60·5	57·8	63·8	62·4	52·0	70·4	67·3	59·0	68·2	64·5
1940	81·7	79·0	79·8	69·6	70·2	66·7	64·4	80·7	71·4	72·4	71·6	65·7	59·2	69·1

TABLE I– *contd.*

Year	Dec.	M.T.B.	Wdn.	D.G.N.	H.P.T.	Ismail	N.W.C.	Belg.	Shik.	Ruia	Khalsa	S.L.D.	Rajkot
1916	56·1	..	..	..	..	..	..	..	..	..	..	..	..
1917	54·7	..	..	..	..	..	..	..	..	..	..	..	..
1918	54·7	..	..	..	..	..	..	..	..	..	..	..	..
1919	72·4	64·3	..	..	..	..	..	..	..	..	..	..	..
1920	65·8	70·7	51·5	..	..	..	..	..	..	..	..	..	..
1921	36·5	62·5	55·0	..	..	..	..	..	..	..	..	..	..
1922	61·2	45·2	51·9	..	..	..	..	..	..	..	..	..	..
1923	67·4	38·6	51·0	50·0	..	..	..	..	..	..	..	..	..
1924	46·7	64·2	59·0	75·0	..	..	..	..	..	..	..	..	..
1925	46·8	47·7	48·1	58·3	63·6	..	..	..	..	..	..	..	..
1926	27·4	41·2	39·0	32·6	35·9	..	..	..	..	..	..	..	..
1927	37·7	35·4	32·5	47·1	43·9	..	..	..	..	..	..	..	..
1928	51·7	49·1	30·1	36·4	42·5	..	..	..	..	..	..	..	..
1929	51·2	37·0	38·0	62·5	40·0	..	..	..	..	..	..	..	..
1930	33·3	35·8	46·7	65·6	40·0	..	..	..	..	..	..	..	..
1931	56·9	57·8	31·0	60·4	38·8	37·5	..	..	..	..	..	..	..
1932	71·9	47·3	38·1	50·0	55·1	57·9	..	..	..	..	..	..	..
1933	38·1	50·0	54·9	40·0	55·1	52·1	62·9	..	..	..	..	..	..
1934	78·9	73·2	68·3	52·2	60·0	51·4	62·1	65·2	41·7	..	..	..	..
1935	..	49·2	52·4	50·9	53·7	66·0	47·2	63·2	55·9	..	..	..	..
1936	..	43·9	62·5	45·1	44·7	41·7	47·3	42·3	58·1	..	..	..	..
1937	..	55·0	54·0	44·8	51·1	69·8	57·4	67·8	41·7	..	..	..	..
1938	..	54·9	76·2	58·5	57·1	65·9	50·0	59·3	56·5	69·0	42·9	58·8	44·4
1939	..	62·5	53·2	60·0	46·4	68·2	67·5	66·3	91·3	62·0	48·6	70·0	46·4
1940	..	61·5	65·7	69·0	55·6	64·4	66·7	89·4	68·3	73·6	63·4	57·1	65·4

TABLE 2

B.A. Examination percentages : 1916 to 1940—Bombay University

Year	Elph.	Wil.	St. X.	Guj.	Raj.	Bar	Fer.	Samal.	D.J.	Bah.	Sir. P.	K.C.	Ex.	Uni.
1916	73·9	70·7	72·9	77·1	..	66·7	61·0	62·5	86·1	75·0	..	..	34·8	63·9
1917	73·8	61·9	70·3	78·1	..	60·0	49·6	78·4	86·4	86·5	..	.	34·7	58·7
1918	77·6	60·8	78·9	58 9	..	59·2	63·5	70·8	69·0	66·1	..	..	40·0	58·4
1919	80·7	62·4	72·3	75·5		63 3	65 4	79·3	72·7	81·7	..	..	47·8	63·4
1920	79·5	68·2	74·6	60·8	..	70·0	62·6	57·7	67·6	85 4	64·7	..	42·1	60·9
1921	80·9	81·5	79·2	84·6	100 0	79·0	73·9	82·4	89·1	72 4	79·6	53·3	47·1	73·6
1922	83·9	82·1	73·6	88 0	60·0	65 0	72·6	68 2	76·1	78 6	66 7	73·3	46·8	71·0
1923	80·4	75 7	79 7	89 1	72 7	63 0	70 3	77 8	89·7	90 5	58 7	73·6	50·9	70·2
1924	87·0	73 4	63 9	71 0	63 3	63 5	61 2	50 0	72·4	75 0	62·5	75 9	31·7	61·4
1925	78·8	53 6	78 7	62 5	56 3	48·8	50·5	87 5	85·7	82·8	56 3	57·6	30·1	54·7
1926	57·1	61·2	65 5	44 6	27·3	45 8	43 6	39 3	49 3	55 9	53 3	43·9	20 5	46·7
1927	80·8	86 4	81 8	91 2	65·8	76·9	73 9	58·8	75 0	86 7	72 7	57 5	53·4	71·4
1928	81·4	75·6	71 4	71 0	66 7	70 2	75 3	68 4	57 6	58 3	64·9	63·3	25·7	61·3
1929	82 3	70 1	64 6	78 8	66 7	69 4	57 7	100 0	79 2	70 0	75·4	65 7	43 9	66·8
1930	78·7	80 4	67 6	79 1	60 0	70 3	70 0	93 8	68 1	62·5	69·4	42·7	38 2	64·4
1931	78·6	86·5	80 0	88·9	72 3	75·3	79·5	87 0	78 3	45·5	68 5	90·7	45 7	70·0
1932	87·7	82 0	73·8	89 4	68·4	68·0	62 0	88 2	86 9	75 0	67·2	79·3	45 7	71·3
1933	88·7	65 3	83 6	83·6	68 5	70 2	71 8	93 2	84·6	65·4	70 0	72 7	40·4	70·1
1934	91·2	79 0	81·0	85 5	79·3	78·1	78 8	90 9	89 7	87 5	75 0	84·6	53·5	77·5
1935	80·0	83 2	80 9	72·7	70 9	70·2	77·0	86 7	78 9	71 4	76·9	69·1	46·9	73·9
1936	86·8	76 5	84·4	84·2	64 6	64 1	77·7	77 3	75 6	54·1	67 7	62 4	51·8	69·2
1937	83·7	92·0	90 3	88·2	73 6	76 1	82·1	84 1	84 8	84 8	86 7	84·4	65·6	82·0
1938	78·4	78·6	81·5	73 7	60·8	61·2	81 0	71 7	82 2	71·9	77·3	82·8	33·8	71·5
1939	80·4	80·4	87·8	76·7	78 1	64·8	74 6	89·0	87 2	81·4	80 1	76·5	58·3	77·3
1940	80·7	86·4	85·9	85·7	745·6	70·0	83·6	87 7	84·7	88·9	79·0	77·5	53·1	78·6

TABLE 2--*contd.*

Year	Dec.	M.T.B.	Wdn.	D.G.N.	H.P.T.	Isml.	N.W.C.	Shik.	Belg.	S.L.D.	Khalsa	Ruia	Non-C.
1916	67·9	..	..	..	..	..	..	..	..	..	..	..	..
1917	47·7	..	..	..	..	..	..	..	..	..	..	..	..
1918	66·0	..	..	..	..	..	..	..	..	..	..	..	..
1919	77·5	..	..	..	..	..	..	..	..	..	..	..	..
1920	52·5		..	..	..	..	..	..	..	..	..	..	..
1921	79·3	..		..	..	..	..	..	..	..	..	..	..
1922	75·0	66·7	..	..	..	..	..	..	..	..	..	..	..
1923	70·0	80·0	75·0	..	.	.	..	..	..	..	..	..	..
1924	68·0	78·6	67·5	..	..	.	..	..	..	..	..	..	..
1925	55·6	63·6	47·4	.	..	..	..	..	..	..	..	..	..
1926	69·7	46·9	39·5	..	..	..	..	..	..	..	..	..	..
1927	81·6	73·5	67·7	..	..	..	..	..	..	..	..	..	..
1928	68·0	76·9	58·5	44·4	90·9	..	..	..	..	..	..	..	..
1929	81·0	82·1	84·6	73·3	70·6	..		..	..	..	..	..	..
1930	61·4	94·7	69·6	63·6	57·9	..	..		..	..	..	..	..
1931	79·5	83·3	68·4	50·0	69·2	..	..		..	..	..	..	..
1932	81·5	82·6	81·3	87·5	66·7	.	.	..	..	..	..	..	..
1933	83·8	58·3	62·9	89·3	85·7	66·7	77·4		..	..	..	..	..
1934	94·7	74·3	78·6	88·9	80·0	77·8	71·1	..	..	..	..	..	..
1935	..	68·9	79·5	81·3	70·3	72·7	74·1	.	..	..	..	..	..
1936	..	60·0	55·0	72·2	66·7	72·7	65·7	75·0	..	..	..	..	50·0
1937	..	82·8	86·0	85·2	91·9	81·3	90·6	100·0	96·2	..	..	..	00·0
1938	..	65·6	77·6	90·6	61·8	93·8	68·9	55·6	74·4	75·0	..	..	100·0
1939	..	77·1	67·7	76·9	74·4	86·5	76·1	87·5	90·6	83·8	33·3	50·0	75·0
1940	..	69·6	84·1	82·1	76·5	85·7	70·9	100·0	73·1	95·7	91·7	71·9	100·0

TABLE 3

I.Sc. Examination percentages : 1916 to 1940—Bombay University

Year	Elph.	Wil.	St.X.	Guj.	Bar.	Fer.	D.J.	Ex.	Uni.	K.C.	Raj.	Samal.
1916 ..	66·7	37·0	61·5	36·4	42·9	53·8	33·3	20·0	46·2	..	..	..
1917 ..	75·0	50·0	50·0	42·9	46·2	45·5	42·9	27·3	46·0	..	..	..
1918 ..	63·6	47·9	42·3	20·0	71·4	46·3	00·0	33·3	45·2	..	..	..
1919 ..	70·0	70·0	59·3	80·0	62·5	62·1	60·0	85·7	67·2	..	..	..
1920 ..	44·4	57·1	50·0	56·7	54·5	52·4	63·6	69·2	54·9	..	..	..
1921 ..	64·3	50·0	55·8	82·6	46·7	43·8	50·0	35·3	52·1	..	..	..
1922 ..	57·9	34·5	50·0	41·7	42·9	57·0	44·4	40·7	49·0	..	..	..
1923 ..	70·0	47·5	62·3	47·1	50·0	48·6	52·6	45·7	51·5	..	..	..
1924 ..	66·1	48·4	42·4	56·2	31·1	40·9	39·7	33·3	43·3	..	..	..
1925 ..	51·8	53·7	48·4	70·2	51·6	51·8	58·3	52·5	53·4	51·1	..	..
1926 ..	51·6	38·0	30·6	46·2	36·6	47·2	47·4	31·3	42·2	50·0	..	..
1927 ..	66·1	41·7	28·2	67·9	40·3	46·6	51·8	41·8	46·4	60·7	..	..
1928 ..	57·6	60·2	70·5	64·0	63·9	57·3	53·5	42·0	54·0	75·0	45·5	..
1929 ..	60·0	52·4	54·8	49·3	67·1	48·0	45·9	51·4	51·5	65·9	27·3	..
1930 ..	56·1	58·4	76·5	61·5	57·0	50·0	61·0	54·1	55·8	47·8	54·5	..
1931 ..	65·2	61·5	53·5	71·4	50·9	47·7	39·1	61·8	50·8	33·9	28·6	..
1932 ..	76·4	61·1	68·5	55·7	66·0	55·5	56·1	62·7	60·3	54·3	63·0	..
1933 ..	62·5	54·5	68·0	60·0	48·2	36·5	32·1	34·0	43·3	47·2	26·1	28·3
1934 ..	71·2	58·0	41·4	66·7	69·4	39·7	51·0	46·6	49·3	59·3	35·7	68·4
1935 ..	70·3	46·9	39·4	55·7	35·4	34·3	35·7	43·2	41·8	41·4	46·0	55·6
1936 ..	70·9	42·6	36·1	43·8	42·9	33·3	26·6	38·5	39·0	42·7	49·1	28·3
1937 ..	78·7	65·0	55·8	66·3	57·2	50·8	58·0	60·0	57·3	60·0	65·9	69·4
1938 ..	65·3	64·5	60·6	50·8	58·3	57·1	56·8	65·5	57·3	53·5	43·5	53·7
1939 ..	85·6	58·8	68·6	74·0	69·2	63·9	69·4	72·7	68·3	66·7	64·4	72·2
1940 ..	71·7	66·7	74·0	72·3	57·9	63·1	49·1	54·6	60·3	47·9	62·7	62·9

TABLE 3—*contd.*

Year	Sir P.	M.T.B.	Dec.	Wdn.	Isml.	N.W.C.	Bel.	D.G.N.	Ruia	Khalsa	Raj-kot	Shikar.	Bahauddin
1928	32·7	45·5	38·5	..	..	..	..	..	..	..	..	..	..
1929	56·7	33·3	25·0	..	..	..	..	..	..	..	..	..	..
1930	43·8	71·4	36 4	..	..	..	..	..	..	..	..	..	..
1931	53·9	50·0	44·8	..	..	..	..	..	..	..	..	..	..
1932	41·7	64·0	53·1	..	27·3	..	..	..	..	..	..	..	..
1933	37·3	34·5	32·4	35·7	53·1	41·2	..	..	..	..	..	..	..
1934	39·0	42·6	28·6	35·6	36·0	44·9	..	..	..	..	..	..	..
1935	34·7	45·8	..	29·4	50·0	40·4	..	..	..	..	..	..	..
1936	30·6	29·5	..	29·2	52·5	50·0	34·8	26·8	..	..	..	..	..
1937	46·8	60·7	..	28·6	69 6	40·5	50·0	46·2	..	..	..	..	..
1938	50·7	58 6	..	78·6	52 9	48 4	55 6	40·9	38·9	71·4	85·7	44·4	35·7
1939	71·4	56·6	..	61·5	69 6	72·1	71·4	55 9	65·9	61·1	38·1	57·1	78·6
1940	72·6	60·8	..	38·5	61·9	50 0	73 3	39·3	47·3	54·4	50·0	53·3	66·7

TABLE 4

B.Sc. Examination percentages : 1916 to 1940—Bombay University

Year	Elph.	Wil.	St. X.	Guj.	Bar.	Fer.	D. J.	Ex.	Uni.	Sir P.	Raj.	K.C	M.T.B.	Ruia	N.W.C.
1916..	40·0	66·7	100·0	00·0	50·0	80·0	..	..	59·3	..	..	..	..	..	..
1917..	00·0	58·8	83·3	81·8	100·0	17·6	..	33·3	54·8	..	.	..	..	..	..
1918..	85·7	84·6	91·7	71·4	50·0	52·6	100·0	50·0	70·4	.	..	..	..	..	..
1919..	33·3	56·0	76·9	44·4	62·5	73·1	100·0	42·9	62·4	..	..	..	..	..	..
1920..	..	40·0	50·0	92·9	58·8	65·2	(0·0	50·0	56·1	..	..	..	..	..	..
1921..	55·6	66·7	56·3	62·5	60·0	43·5	50·0	35·0	52·7	..	.	..	..	..	..
1922..	75·0	44·4	53·8	69·2	73·3	45·5	33·3	52·2	55·0	.	..	..	..	..	..
1923..	56·3	72·7	70·6	80·0	64·7	52·3	100·0	15·0	57·0	.	.	..	..	..	..
1924..	61·1	57·7	57·1	100·0	60·0	52·1	28·6	32·3	52·5	.	..	..	..	..	..
1925..	67·4	58·3	62·5	50·0	55·6	40·7	40·0	51·3	51·8	..	..	..	..	..	..
1926..	73·2	62·5	74·1	65·4	43·8	44·3	100·0	31·4	53·5	.	..	..	..	..	..
1927..	65·5	60·0	56·0	70·8	88·9	50·5	51·7	55·2	59·0	..	.	..	..	..	..
1928..	75·0	69·4	61·5	73·3	76·0	53·7	77·1	42·7	61·5	.	..	..	..	..	..
1929..	82·5	84·6	53·8	63·6	71·4	55·3	57·1	48·2	61·4	.	..	..	..	..	..
1930..	84·4	76·9	66·7	86·1	76·2	53·4	64·3	52·9	65·2	40·0	..	..	..	..	..
1931..	84·1	86·2	90·0	71·4	82·8	61·9	79·3	57·1	71·0	62·1	..	..	..	..	..
1932..	88·7	89·7	90·3	81·8	75·0	71·8	61·0	48·2	72·4	63·2	75·0	..	..	..	..
1933..	98·4	73·0	92·6	92·6	84·1	61·3	85·7	41·8	72·8	78·3	88·9	..	..	..	..
1934..	90·0	86·7	90·2	88·9	74·6	53·4	71·6	47·4	68·5	65·4	52·4	..	..	..	..
1935..	89·3	86·5	85·7	75·0	76·8	71·4	62·0	32·0	66·6	61·5	71·4	..	..	..	..
1936..	83·0	80·6	91·1	90·2	79·3	67·3	67·9	48·3	70·7	65·7	55·0	79·0	75·0	..	..
1937..	89·5	85·7	86·0	90·6	86·4	71·3	63·3	44·4	70·9	69·6	65·0	92·0	33·3	..	..
1938..	91·0	68·4	84·8	92·3	88·9	72·8	68·2	45·2	74·5	72·7	83·3	87·5	70·6	..	..
1939..	91·9	82·1	90·1	77·5	85·3	75·0	78·6	38·1	75·9	78·1	81·0	80·8	69·0	100·0	..
1940..	88·1	81·6	93·8	90·2	82·0	79·8	83·5	60·2	80·3	66·7	78·9	88·2	73·1	68·8	66·7

TABLE 1-a

Precis, I.A.—1919 to 1938

(i)		(ii)	(iii)	(iv)	(v)	(vi)	(vii)
College		No. passed	No. appeared	True mean	Average percent-age	Excess of (v) over (iv)	Variance s^2
E. C.	..	1132	1624	69·70	70·85	+1·15	60·14
Wil.	..	1625	2566	63·33	63·27	—0·06	103·50
St. X.	..	2308	3884	59·42	58·36	—1·06	92·07
Guj. C.	..	1269	2124	59·74	59·57	—0·17	171·79
Raj. C.	..	862	1909	45·15	45·13	—0·02	112·75
Bar. C.	..	1528	2978	51·31	52·08	+0·77	94·90
F. C.	..	1673	2952	56·67	55·44	—1·23	115·41
Samal.	..	771	1271	60·66	58·10	—2·56	196·66
D. J.		967	1804	53·60	53·88	+0·28	127·18
Bah. C.	..	593	1016	58·37	58·14	—0·23	59·14
Sir P.	..	1365	2445	55·82	55·94	+0·12	132·31
K. C.	..	926	1881	49·23	51·03	+1·80	150·50
Ex.	..	3959	9222	42·93	43·20	+0·27	69·57
Total	..	18978	35676	53·19	55·77	+2·58	..

TABLE 2-a

Precis, B.A.—1921 to 1940.

(i)		(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
College		No. passed	No. appeared	True Mean	Average percent-age	Excess of (v) over (iv)	Variance s^2	Correlation co-efficient
E. C.	..	1169	1434	81·52	81·37	—0·15	46·75	+0·14
Wil.	..	1472	1887	78·01	77·49	—0·52	85·52	+0·09
St. X.	..	1978	2491	79·41	77·76	—1·65	60·90	+0·44
Guj. C.	..	1100	1396	78·79	79·42	+0·63	128·55	+0·01
Raj. C.	..	740	1082	68·39	67·49	—0·90	178·32	+0·37
Bar. C.	..	1252	1853	67·57	67·49	—0·08	75·22	—0·18
F. C.	..	1639	2304	71·14	70·85	—0·29	114·39	—0·08
Samal.	..	614	756	81·22	79·10	—2·22	242·54	—0·15
D. J.	..	1014	1282	79·09	78·75	—0·34	113·21	+0·17
Bah. C.	..	382	523	73·04	72·93	—0·11	163·43	+0·35
Sir P.	..	1165	1611	72·31	70·39	—1·92	74·55	+0·03
K. C.	..	765	1085	70·51	69·34	+1·17	178·55	+0·03
Ex.	..	1760	3898	45·15	44·15	—1·00	129·18	+0·35
Total	..	15050	21602	69·67	72·04	+2·37	..	+0·09

TABLE 3-a

Precis, I.Sc.—1919 to 1938

(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
College	No. passed	No. appeared	True mean	Average percentage	Excess of (v) over (iv)	Variance s^2
E. C. ..	723	1114	64·90	63·82	−1·08	75·68
Wil. ..	866	1645	52·64	53·30	+0·66	90·94
St. X. ..	1165	2268	51·37	52·60	+1·23	178·80
Guj. C. ..	703	1189	59·12	59·69	+0·57	132·79
Bar. C. ..	933	1798	51·89	51·62	−0·27	124·93
F. C. ..	2099	4473	46·93	48·03	+1·10	72·60
D. J. ..	1027	2159	47·57	49·18	+1·61	104·44
Ex. ..	1389	2858	48·60	49·76	+1·16	201·83
Total ..	8905	17504	50·87	53·50	+2·77	..

TABLE 4-a

Precis, B.Sc.—1921 to 1940

(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
College	No. passed	No. appeared	True mean	Average percentage	Excess of (v) over (iv)	Variance s^2	Correlation co-efficient r
E. C. ..	827	989	83·62	79·49	−4·13	160·52	+0·27
Wil. ..	441	589	74·87	73·68	−1·19	155·82	+0·25
St. X. ..	672	813	82·66	75·35	−7·31	238·27	+0·29
Guj. C. ..	428	534	80·15	78·57	−1·58	165·74	−0·16
Bar. C. ..	578	733	78·85	74·25	−4·60	144·74	+0·27
F. C. ..	1103	1819	60·64	58·86	−1·78	140·68	−0·34
D. J. ..	490	706	69·40	66·16	−3·24	381·02	−0·26
Ex. ..	658	1441	45·66	43·94	−1·72	117·32	+0·31
Total ..	5197	7624	68·17	68·79	+0·62	..	+0·08

PRODUCT OF TWO DEMLO-NUMBERS OF THE TYPE (R)N × (R')N' WHERE N AND N' ARE UNEQUAL

By

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(1) The case for $n = n'$ has been considered in the *Bombay University Journal* of November 1939. In order to find

$$(r)_n \times (r')_{n'} = (1)_n \times (1)_{n'} \times rr'$$

we first consider the case $(1)_n \times (1)_{n'}$ where $n > n'$. In the article referred to above the product $(1)_{n'} \times (1)_{n'} = (1)_{n'}^2$ has been already discussed. This is essential for the present discussion.

(2) In order to put down the value of say $(1)_{17} \times (1)_{23}$ or $(1)_{20} \times (1)_{15}$ it will be first necessary to write down the value of $(1)_{17}^2$ or $(1)_{15}^2$ whichever is smaller n or n' the corresponding value of $(1)_n^2$ or $(1)_{n'}^2$ is the essential value first required. We shall always take $n > n'$ and hence $(1)_{n'}$ will be called the *lower element* and $(1)_n$ as the higher. With this product obtained the product of the two elements $(1)_n \times (1)_{n'}$ can be simply put down by repeating some number of times some digits in the square of the lower element. Theoretical discussion of the reasons is given elsewhere. The following is the outline of the results obtained.

(3) Product of $(1)_n \times (1)_{n'}$ when $n' \leqslant 9$.

Here we write the value of $(1)_{n'}^2$ and note the highest digit in this product. This digit will be called as the *maximum reach*. In the product for $(1)_{n'}^2$ repeat this digit of maximum reach as often as $n - n' + 1$ times and we get the required product, e.g., take $(1)_{12} \times (1)_7$. Here $n' = 7$ $n - n' + 1 = 6$ $(1)_7^2 = 1234567654321$. 7 is the maximum reach.

∴ The product is = 123456(7)₆654321.

As another example take $(1)_{14} \times (1)_6$. Here $n' = 6$ is the maximum reach and $n - n' + 1 = 9$ and therefore the product is

    12345(6)₉954321.

(4) Product of $(1)_n \times (1)_{n'}$ when $n' = 10$. Here it is obvious that $n > 10$. Investigation gives the following method of writing the product. In $(1)_{n'}^2$ the Lgr is 123456790 and Rgr is 098765432. Repeat the digit 1, $(n - n')$ times in the middle portion and the whole followed by the digit 1 in the units place. Thus in $(1)_{17} \times (1)_{10}$, $n - n' = 7$ and the product is

    123456790 (1)₇ 0987654321.

Similarly in $(1)_{12} \times (1)_{10}$, $n - n' = 2$ and the product is 123456790 (1)₂ 0987654321.

(5) Product of $(1)_n \times (1)_{n'}$ when n' is of the form $9m + 1$. In this case the digit one appears repeated $(n - n')$ times and will have the

constant Lgr 123456790 on the left and the constant Rgr 098765432
on the right : but these constants will be repeated m times. Of course
we put the digit one at the end thus completing the process. Thus in
$(1)_3 \times (1)_{28}$ $n' = 28 = 9 \quad 3 + 1$, n - n'   4 and therefore the
product is obtained by taking Lgr, Rgr, repeated 3 times and 1 repeated 4
times in the centre. Thus the product will be

$$(123456790)_3 \ (1)_4 \ (098765432)_3 1.$$

(6) Product of $(1)_n \times (1)_{n'}$ when $n' > 10$ but not of the form 9m + 1.

In this case first we write the value of $(1)_n^2$ in accordance with the
article already referred to and note the highest digit in the neighbourhood
of the middle called the maximum reach. This digit is repeated
$n - n' \cdot 1$ times instead of writing it only once and we get the product,
e.g., $(1)_{19} > (1)_{14}$. Here n' 14 n - n' = 5 and n - n' 1 6.
Now we have $(1)_{14}^2 =$ 123456790 123454320987654321. In this case
the middle digit is 5 and we repeat it 6 times and we have the product

$$1234567901234(5)_6 4320987654321.$$

Take the product $(1)_{33} \times (1)_{22}$. Here n - n' 1 12. The value
of $(1)_{22}^2$ $(123456790)_2$ 123432 $(098765432)_2 1$. The maximum reach in
the middle is 4 and this is repeated 12 times, giving the product
$(123456790)_2$ 123 $(4)_{12}$ 32 $(098765432)_2 1$.

Thus we get the value of $(1)_n \vee (1)_{n'}$. We multiply this product by
rr' and get the required general product. We consider this according
to the different cases that arise.

(7) In writing down the product of $(r)_n$ $(r')_n$ we first write down the
product of $(r)_{n'}$ $(r')_n$ n > n', i.e., rr' $(1)_n^2$ in accordance with the
methods described in the article referred to in the beginning. It has been
pointed out there that the product is $(lgr)_K$ L $(rgr)_K$ R where the values
of lgr, rgr L and R are found out from the arguments rr' and ⋌ by using
the tables given at the end of that article   The unit digit of the number so
obtained forms R and the remaining part gives us L. Thus by referring
to Table No. II for arguments rr'   35 and ⋌ 3 we find the number
431235 of this 5   R and 43123   L. Similarly for arguments
rr'   8 and ⋌ 7 we get the number 9876541234568 of which
8   R and L   987654123456. Having determined this value
of L in any particular case partition it into two parts thus. If L contains
even number of digits, say 2m, then let the two parts be L' and L″, each
of digits m. If L contains odd number of digits, say (2m - 1), then let
the part L' be of (m 1) digits and the part L″ of m digits ; e.g., for the
first value of L given above, viz., 43123 the digits are odd 5. Hence
L' = 431 and L″ 23. Again for the second value of L above
987654123456 the digits are even 12. Hence L' 987654 and L″ =
123456. Thus the product rr' $(1)_n^2$ would now be expressed as
$(lgr)_K$ L'—L″ $(rgr)_K$ R written in order. This may be referred to as
partition of L.

(8) We shall define one more term. This will be called the *digital
root of any given number*. If all the digits of any given number are added
together and the sum again and again treated in the same way ultimately

we get a single digit number $\leqslant 9$. This will be the digital root of that quantity, e.g., 7235 has the sum of digits 17 ; his again has sum of digits 8. This is digital root of 7235. It is obvious that the digital root is the remainder when the given number is divided by 9. It is also well known that the digital root of the product of two numbers is equal to the digital root of the product of the digital roots of the two numbers.

(9) The product $rr' \times (1)_n \times (1)_n$, i.e.. $(r)_n \setminus (r')_{n'}$. Our investigation gives the following method of putting down the product.

First find the value of rr' $(1)_n^2$ and write it as $(lgr)_k$ $L' - L''$ $(rgr)_k$ R with a gap between L' and L''. Insert within this gap the digital root of n' rr', $(n$ $n')$ times and we get the required product.

Thus to find $(5)_{14} \times (7)_{12}$. Here $rr' = 35$, n' 12, n 14, $n - n'$ 2, K 1, α 3. Arguments rr' - 35 and α - 3 give 431235 ; R - 5, L -- 43123, L' - 431, L'' 23, digital root D of the product rr' $\times$ n', i.e. 35×12 8×3 24 6.
lgr 432098765, Rgr - 456790123.
Hence the product is

$$(432098765) \ 431 \ (6)_2 \ 23 \ (456790123)5.$$

It will be noted that except for the repetition of the gap number the product depends only on the lower element. Thus the product $(5)_{19} \times (7)_{12}$ is given by

$$(432098765) \ 431 \ (6)_7 \ 23 \ (456790123)5$$

for the only value that changes is n n' 7. The general formula for the required product therefore can be put down as

$$(lgr)_k \ L' \ (D)_n \ , \ L'' \ (rgr)_k \ R$$

with the notation that we have been using. We shall take a few examples to illustrate the peculiarities of the different cases hat arise.

(10) $(5)_{19} \times (3)_{14}$. Here rr' 15 multiple of 3. $n' - 14$, K - 4, $\propto$ 2. Table I for arguments 15, 2 gives 1815. Hence R 5, L' 18, L'' - 1, lgr = 185, Rgr - 481, D - 15 14 6 $\times$ 5 30 - 3, $n - n'$ 5 and therefore the product is

$$(185)_4 \ 18 \ (3)_5 \ 1 \ (481)_4 \ 5.$$

$(7)_{16} \times (4)_8$. Here rr' - 28, n' 8, K -- 0, $\propto$ - 8. Table II gives the value

$$34567900054320988$$

of which R 8 and the remaining gives

$$L' - 34567900, \ L'' - 5432098$$

D = 28×8 - 8, n - n' = 8 and hence because these are no values of lgr and rgr, the product is

$$34567900 \ (8)_8 \ 5432098 \ 8.$$

Take another example $(8)_8 \times (3)_{11}$. Here rr' 24 a multiple of 3. Hence K = 2, $\propto$ - 2. Table I gives the value 2904. R - 4, L' = 29, L'' = 0, D = 3, $n - n' = 3$ and lgr = 296, rgr = 370. Hence the product is

$$(296)_2 \ 29 \ (3)_3 \ 0 \ (370)_2 \ 4.$$

(11) It has been shown while discussing the product of linear demlo-numbers that rr' can only have the following 36 values: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 16, 18, 20, 21, 24, 25, 27, 28, 30, 32, 35, 36, 40, 42, 45, 48, 49, 54, 56, 63, 64, 72, 81. Of these rr' = 1 need not be taken into account for that only gives the product of $(1)_n \times (1)_{n'}$. Cases of rr' = 10, 20, 30, 40 are practically the cases of 1, 2, 3, 4 with a zero at the end and thus do not practically give us any new discussion. rr' = 9, 18, 27, 36, 45, 54, 63, 72, 81 are special cases and will require a special treatment given later. (See paragraph 15). Out of the 36 values of rr' we need therefore take only 22 cases when the 14 already mentioned are excluded.

The repeating digit D is found from rr' × n' by taking the digital root of this product. It is easily seen that n' may be increased or decreased by nine or any multiples of 9 and the digital root of the product remains the same. Hence for finding the digital root, n' can only take 9 values and thus in finding the digital root of rr' × n' (as rr' can only take 22 values and n' only 9) only 22 × 9 = 198 cases might arise. Of these the product in 37 cases has to be specially treated. In the remaining 161 cases the product is to be written out as explained in paragraph 9. Examples given in paragraph 10 all three belong to this latter simple class.

(12) The 37 cases which require a special treatment are indicated with a + sign for the arguments rr' and n'.

n' =	1	2	3	4	5	6	7	8	9
rr' =									
14		$+_1$							
16				$+_1$					
25				$+_1$				$+_2$	
28	$+_1$	$+_2$	$+_3$						
32		$+_1$		$+_2$		$+_3$			
35						$+_9$	$+_2$	$+_1$	
42		$+_3$			$+_3$			$+_1$	
48	$+_3$			$+_9$		$+_3$			
49	$+_4$		$+_9$		$+_2$		$+_1$	$+_5$	
56	$+_2$	$+_4$	$+_6$		$+_1$	$+_3$	$+_5$		
64	$+_1$	$+_2$	$+_3$	$+_4$	$+_5$	$+_6$	$+_7$		

e.g., the case rr' = 48, n' = 4, 13, 22, etc., is a special case. The figure near the +ve sign shows the value of the digital root of this product. Thus in the case above cited 48 × 4 = 12 × 4 = 3 × 4 = 12 = 3 is the digital root.

(13) In these special cases the product of $(r)_n \times (r')_{n'}$ is given by $(lgr)_k$ $(L' + 1)$ (D) $n - n' + 1$ $(D - 1)$ L'' $(rgr)_k$ R. The method may be thus explained. As before find the values including D to be repeated $n - n'$ times. Instead of writing the last value of D write this as $D-1$ and add 1 to the value of L' already obtained. Thus the case may be denoted by $(+ 1 - 1)$ type. All the 37 cases mentioned belong to this class. We shall take a few examples in illustration. A theoretical discussion is being prepared and will be given later.

(14) $(7)_{17} \times (4)_{12}$. Here $rr' = 28$, $n' = 12$ (i.e., 3 for the table given before). This is $(+ 1 - 1)$ type. $K = 1$, $\alpha = 3$. Table gives lgr = 345679012, rgr = 765432098 and arguments 28, 3 give 344988. Hence R = 8, L' = 344, L'' = 98. Digital root of product $28 \times 12 = 3$. $n - n' = 5$. Hence instead of writing 33333 between the gap $L' - L''$ we write 33332 and add 1 to L' making it 345. Thus the required product is

$$(345679012)\ 345\ 33332\ 98\ (765432098)8.$$

Consider $(8)_{15} \times (7)_{10}$. Here $rr' = 56$, $n' = 10$ (i.e., 1 for reference). This is $(+ 1 - 1)$ type. $K = 1$, $\alpha = 1$. Table gives lgr = 691358024, rgr = 530864197; arguments 56, 1 give 56. Hence R = 6, L' = 5, L'' does not exist. $D = 2$, $n - n' = 5$. Hence instead of writing 22222 we write 22221 and L' becomes 6. Thus the product is

$$(691358024)6\ \underline{22221}\ (530864197)6.$$

(15) When rr' is a multiple of 9 the product $(r)_n \times (r')_{n'}$ is peculiar and can be very easily written out. rr' is a multiple of 9 and can have the following values written thus to make these quantities each of two digits

09, 18, 27, 36, 45, 54, 63, 72, 81   (i)

These increased by nine would give the following

18, 27, 36, 45, 54, 63, 72, 81, 90   (ii)

in order. We denote any quantity of the (i) set by ab where a, b are the two digits from left to right. A corresponding quantity of the second (ii) set is denoted by a' b' in the same way. Thus it can be shown that $(r)_n \times (r')_{n'}$ is given by

$(a')_{n'-1}$ a $(9)_n$ n' (b') $n'-1$ b.

It may be said that a' = lgr, b' = rgr, K = n' - 1.

L' = a, L'' does not exist and 9 is the digital root, e.g., take $(6)_8 \times (3)_{11}$. Here $rr' = 18 = ab$ $a'b' = 27$. $n' = 8$, $n - n' = 3$, $n' - 1 = 7$. Hence the product is

$(2)_7$ 1 $(9)_8$ $(7)_7$ 8
= 2222222199977777778.

Take $(9)_{15} \times (7)_{10}$. Here $rr' = 63 = ab$, $a'b' = 72$, $n' = 10$, $n - n' = 5$ $n' - 1 = 9$. Hence the product is

$(7)_9$ 6$(9)_5$ $(2)_9$ 3.

Take the case of $(1)_7 \times (9)_{13}$. Here $rr' = 09 = ab$, $a'b' = 18$, $n' = 7$, $n - n' = 6$, $n' - 1 = 6$. Hence the product is

$(1)_6$ 0$(9)_6$ $(8)_6$ 9.

For ready reference a table of digital roots is given for the 22 values mentioned before   The underlining shows that the cases belong to the $(+1-1)$ type.

Table of digital roots for $rr' \times n'$

Value of rr'	1	2	3	4	5	6	7	8	9
2	2	4	6	8	1	3	5	7	9
3	3	6	9	3	6	9	3	6	9
4	4	8	3	7	2	6	1	5	9
5	5	1	6	2	7	3	8	4	9
6	6	3	9	6	3	9	6	3	9
7	7	5	3	1	8	6	4	2	9
8	8	7	6	5	4	3	2	1	9
12	3	6	9	3	6	9	3	6	9
14	5	<u>1</u>	6	2	7	3	8	4	9
15	6	3	9	6	3	9	6	3	9
16	7	5	3	<u>1</u>	8	6	4	2	9
21	3	6	9	3	6	9	3	6	9
24	6	3	0	6	3	9	6	3	9
25	7	5	3	<u>1</u>	8	6	4	<u>2</u>	9
28	<u>1</u>	<u>2</u>	<u>3</u>	4	5	6	7	8	9
32	5	<u>1</u>	6	2	7	<u>3</u>	8	4	9
35	8	7	6	5	4	<u>3</u>	<u>2</u>	<u>1</u>	9
42	6	<u>3</u>	9	6	<u>3</u>	9	6	<u>3</u>	9
48	<u>3</u>	6	9	<u>3</u>	6	9	<u>3</u>	6	9
49	<u>4</u>	8	<u>3</u>	7	<u>2</u>	6	<u>1</u>	<u>5</u>	9
56	<u>2</u>	<u>4</u>	<u>6</u>	8	<u>1</u>	<u>3</u>	<u>5</u>	7	9
64	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	8	9

The *underlined* figures are digital roots of $(+1-1)$ type.   Others not underlined are of ordinary type.

There are only 37 cases of $(+1-1)$ type.   All other 161 are of simple type.

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    Khare's Wada, Camp Deolali.

X-RAY ANALYSIS OF SOME ORGANIC COMPOUNDS

By

R. H. Joshi and M. R. Kapadia

Abstract

Crystals of acetanilide, methyl acetanilide and p—acetaniside have been studied by the rotating crystal method. The dimensions of the unit cell. the number of molecules in the cell and the space group to which the crystals belong are determined

ACETANILIDE

ACETANILIDE crystallises from alcohol in thick plates parallel to the c (001). The crystals belong to the orthorhombic bipyramidal class and have been found to develop the following faces :—

c (001), q (012), o (111), a (100)

The axial ratio determined from crystallographic measurements is a : b : c=0˙8421 : 1 : 2˙0671

(cf. Groth, Chem. Kristallg., IV, p. 225)

Rotation and oscillation photographs were taken about a, b and c axes using Cu, K—radiation.

The lengths of the axes as determined from rotation photographs are a= 7˙95 A°, b=9˙48 A° and c 19˙56 A°. The axial ratio, therefore, is

a : b : c =0˙8397 : 1 : 2˙063

This agrees well with that given in Groth (loc. cit.). The number of molecules in the unit cell as calculated from the above values and the specific gravity of the crystals (1˙219, Groth, loc. cit.) is nearly 8 (exactly 8˙017). The indices of the planes appearing in the various oscillation photographs were obtained by the aid of Bernal's chart. The list of planes observed is given in tables I and II. The intensities of the planes were determined by eye estimation and the symbols used have the usual meaning.

TABLE I

Axial planes	Prism planes (okl)	Prism planes (hol)	Prism planes (hko)
002 s.	012 m.s.	201 s.	120 v.s.
004 m.	014 m.	202 s.	140 m.s.
008 v.w	016 w.	203 m.s.	220 m.s
00 (10) w.	01 (10) w.	204 m.	240 v.w.
020 m.s.	022 v w	205 v.w.	320 v.w.
040 w.m.	024 v.w.	206 w.	
200 v.w.	026 v.w.	207 w.m.	
400 v.w.	032 v.w.	208 v.w.	
	034 v.w.	209 v.w.	
	036 v.w.		
	046 v.w.		

TABLE II

GENERAL PLANES

Axial planes		Prism planes (okl)	Prism planes (hol)	Prism Planes (hko)
111 m.s.		211 m.s.	311 s.	411 v.w.
112 m.s.		212 s.	312 m.s.	412 v.w.
113 m.		213 m.s.	313 w.	413 v.w.
114 m.		215 v.w.	315 v.w.	415 v.w.
115 m.		216 w.	317 v.w.	422 v.w.
116 w.		217 v.w.	321 w.	423 v.w.
117 w.		221 m.s.	322 v.w.	
118 w.		223 w.	323 w.m.	
119 v.w.		224 m.	324 w.m.	
121 s.		225 w.	325 v.w.	
122 m.		227 m.	326 v.w.	
123 w.		228 v.w.	327 v.w.	
124 w.m.		229 v.w.	331 w.	
125 w.m.		233 v.w.	332 v.w.	
126 w.		241 v.w.	333 v.w.	
127 w.		242 v.w.	334 v.w.	
132 m.		243 v.w.	341 v.w.	
133 v.w.		244 v.w.	343 v.w.	
135 w.				
136 w.				
138 v.w.				
141 v.w.				
142 m.				
145 w.				
151 v.w.				
152 v.w.				
153 w.				

It will be seen from the list of planes that (hol) planes are halved when h is odd, (okl) planes are halved when l is odd and (hko) planes are halved when kh is odd. These halvings assign the crystals of acetanilide to the space group Q_h^{15} (D_{2h}^{15} Pbca) (cf. Astbury and Yardley, Phil. Trans., 1924, A, 224, 235). The number of molecules required by the space group is eight. Thus, the molecules of acetanilide are asymmetric which is also expected from the graphical representation of the molecule.

Methyl acetanilide

Methyl acetanilide crystallises from alcoholic solutions in the form of long thick crystals which develop the c (001) face prominently, the long edge being parallel to the b—axis. The faces which have been found to develop on the crystals are as follows :—

c (001), q (012), r (101), m (110)
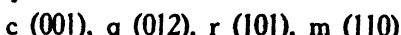
The crystals belong to the rhombic class and the axial ratio is given by

$$a : b : c = 0.9293 : 1 : 2.3486$$

(cf. Groth, Chem. Kristallg., IV, p. 244)

The lengths of the axes obtained from the rotation photographs about a, b and c axes are

$$a = 6.56 A°, b = 7.06 A° \text{ and } c = 16.56 A°$$

The axial ratio is a : b : c=0·9292 : 1 : 2·346 which agrees well with that given in Groth. The list of planes obtained from oscillation photographs is shown in tables III and IV.

TABLE III

Axial planes	Prism planes (okl)	Prism planes (hol)	Prism planes (hko)
003 m.s.	012 s.	101 s.	110 s.
005 w.m.	013 s.	102 m.s.	120 w.m.
008 w.	014 m.s.	103 m.s.	130 w.
00 (11) w.	015 w.	104 m.s.	210 w.
020 s.	016 m.	105 w.	220 w.
040 m.	017 v.w.	106 m.	310 w.
200 m.s.	018 w.	107 w.	
	01 (10) v.w.	108 m.	
	022 m.s.	201 s.	
	023 s.	202 m.	
	024 s.	203 m.s.	
	025 w.m.	204 m.	
	026 m.s.	205 m.s.	
	028 v.w.	206 w.	
	02 (10) w.	207 w.m.	
	032 w.	209 w.	
	033 v.w.	301 w.	
	034 m	302 w.m.	
	035 v.w.	304 m.	
	042 w.		

TABLE IV

GENERAL PLANES

Axial planes	Prism planes (ok)	Prism planes (hol)	Prism planes (hko)
111 s.	211 s.	311 w.	
112 s.	212 w.m.	312 w.	
113 m.s.	213 w.m.	313 w.	
114 m.s.	214 w.	314 v.w.	
115 v.w.	215 w.	315 v.w.	
116 w.m.	216 w.m.	316 w.	
117 w.	219 w.	323 m.	
121 s.	221 w.	326 w.	
122 w.	222 v.w.	334 w.	
123 v.w.	223 w.		
124 w.	224 w.		
125 v.w.	228 w.		
126 w.	231 w.		
128 w.			
129 v.w.			
131 w.			
132 m.			
133 m.			
134 w.m.			
135 w.m.			
141 w.			

It will be seen from the list that (100) and (010) planes are halved since only (200) and (020) and (040) planes have been observed. With

the data available at present, it can only be inferred that the crystal belongs to the space group Q^3 in the bisphenoidal class. However, it may happen that these halvings do not hold in case of higher orders of (100) and (010) planes. In such a case there will be no halvings and the crystal may belong to (*i*) bisphenoidal class, and the space group Q^1 or (*ii*) pyramidal class and the space group C^1_{2v}.

The number of molecules required by the space group is 4. The number of molecules calculated from the dimensions of the unit cell and the specific gravity of the crystals (1·288 determined in the laboratory by floatation method) comes out to be nearly 4 (exactly 3·998). The molecules of methyl acetanilide are also, therefore, asymmetric which is also expected from the graphical representation of the molecule.

p—Acetaniside

p—Acetaniside crystallises from alcohol. The following faces are developed :—

$$a\ (100),\ m\ (110),\ c\ (001),\ o\ (111)$$

The crystals belong to the rhombic bipyramidal class and the axial ratio calculated from the crystallographic measurements is given by—

$$a : b : c = 1\cdot3490 : 1 : 0\cdot8304$$

(cf. Groth, Chem. Kristallg., IV, p. 241)

Rotation photographs taken about a, b and c axes give the following values for the lengths of the three axes :—

$$a = 24\cdot44\ A°,\ b = 9\cdot08\ A°,\ c = 7\cdot54 A°$$

The axial ratio is a : b : c = 2·692 : 1 : 0·8305 which agrees well with that given in Groth except that a axis is doubled.

The reflecting planes identified on various oscillation photographs are shown in Tables V and VI.

TABLE V

Axial planes	Prism planes (hol)	Prism planes (okl)	Prism planes (hko)
002 m.	102 m.s.	021 s.	210 v.s
020 m s.	202 s.	022 m s	220 w.m.
200 s.	204 w.	023 w.	230 w.
400 s.	302 s	041 m s	240 m
600 w.m	402 m.	042 w.m.	410 m
800 m.	404 w.		420 m.
(10) 00 w.	502 m.		430 w.
(12) 00 w.	602 w.		440 v.w
	702 w.m		450 w.
	802 w.		610 m.s.
	902 w.		620 m.
	(10) 02 w.m.		630 m.
	(11) 02 w.		640 m.
	(12) 02 w.		810 s.
			820 m.s.
			830 v.w.
			840 v.w.
			(10) 10 w.m.
			(12) 10 w.m.
			(12) 20 w.

TABLE VI

GENERAL PLANES

111 s.	311 m.	512 m.	711 m.s.	912 m.	(11) 11 w.
112 m.s.	312 m.	521 m.	712 w.m.	931 v.w.	(11) 12 w.
113 w.m.	313 w.	522 m.	713 w.	932 v.w.	(11) 21 w.
114 v.w.	314 v.w.	523 v.w.	721 m.	(10) 11 m.	(11) 22 v.w.
121 s.	321 w.m.	531 v.w.	722 m.	(10) 12 v.w.	(12) 11 w.m.
122 s.	322 w.m.	532 w.	723 v.w.	(10) 21 v.w.	
123 w.	323 m.s.	541 v.w.	731 v.w.	(10) 22 v.w.	
131 w.m.	331 m.s.	542 v.w.	732 v.w.	(10) 32 v.w.	
132 w.m.	332 m.	551 w m.	741 v.w.		
133 m.s.	333 m.	611 m.	811 m.		
141 w.	341 m.	612 m.	812 s.		
143 w.m.	342 w.	621 w.	813 s.		
211 s.	351 v.w.	622 v.w.	814 v.w.		
212 m.s.	411 w.	623 w.m.	821 m.		
213 m.	414 w.	624 v.w.	822 m.		
214 w.	421 m.s.	631 w.	823 v.w.		
221 m.s.	422 m.	641 v.w.	831 w.		
222 w.m.	423 m.		832 v.w.		
223 m.	424 v.w.		841 w.		
224 w.m.	432 v.w.				
231 m.s.	433 m.s.				
233 m.s.	441 m.				
241 w.					
242 w.					
251 w.					

It can be seen from these tables that (okl) planes are halved when k is odd, (hol) planes are halved when l is odd and (hko) planes are halved when h is odd. There are no halvings in the general planes. These halvings fix up the space group Q^{15}_h for the crystal (cf. Astbury and Yardley, loc. cit.).

The number of molecules required by the space group in the unit cell is 8. The number of molecules calculated from the cell dimensions and the specific gravity which was found to be 1·32, comes out to be nearlv 8 (8·065 exactly). In this case, also, therefore, the molecules are asymmetric.

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS

Part VIII—Colloidal Ceric Hydroxide

By

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IN Part VII [Vora, Barve and Desai, *Proc. Indian Acad. Sci.*, 1941, *13*, 100] of this series measurements of cataphoretic speed (cat. speed) in the presence and absence of electrolytes, stability and conductivity of colloidal zinc ferrocyanide were given. In the present paper similar measurements obtained with colloidal solution of ceric hydroxide are presented.

EXPERIMENTAL

Ceric hydroxide sol was prepared in the following manner :

20 gm. of ceric ammonium nitrate were dissolved in distilled water and ceric hydroxide was precipitated by adding excess of ammonia. The precipitate was washed free from ammonia with hot water and suspended in one litre of distilled water. The suspension was boiled and continuously stirred, and at intervals of a few minutes, 2 to 3 c.c. of 2N.HCl were added to it. Evaporated water was replaced by addition of distilled water from time to time. After three to four hours' heating, clear fluorescent golden yellow ceric hydroxide sol was obtained.

The sol was dialysed in parchment paper bags in the usual manner and samples were removed for experiments after different periods of dialysis. Dialysis was carried out in a dark room to avoid effect of light on the sol. During dialysis HCl was detected in the dialysate; some cerium was also detected in the dialysate in the beginning. The concentration of the colloid was determined by precipitating it with ammonium chloride and weighing finally as ceric oxide, from time to time and was found to remain constant after five days' dialysis. All the experiments with the same sample of the sol were carried out in as short a time as possible to minimise effect of ageing.

The cat. speed and conductivity were determined as before. Dialysate made equiconducting with the sol by the addition of HCl was found to be a satisfactory upper liquid in cat. speed experiments. In studying the effect of electrolytes on the colloid, the electrolytes were also added to the upper liquid so as to get the same ionic environment. The difference between the direct and reverse movements of the boundary never exceeded 5 per cent.

The stability of the sol was determined by finding out the amount of NH₄Cl necessary to give instantaneous coagulation as judged by the naked eye when the tube was held against a transluscent back ground illuminated by a lamp.

Experiments on ageing and exposure to sunlight were carried out as in the previous work.

Viscosity was determined by means of Ostwald Viscometer.

All the experiments were carried out at a temperature of 30°C.

RESULTS AND DISCUSSION

In all the tables cat. speed (mean of direct and reverse movements) is corrected for viscosity and expressed in centimetres per second per volt per centimetre $\times 10^5$. In the experiments on the effect of electrolytes on the colloid, the concentration of the electrolyte is expressed in millimoles per litre of the mixture colloid + electrolyte + water.

Dilution is expressed in terms of the ratio

$$\frac{\text{Volume of the diluted sol}}{\text{Volume of the original sol}};$$

the original sol has thus dilution 1.

Flocculation values (F. V.) are expressed in millimoles of the electrolyte per litre of the mixture.

The viscosity results are expressed in terms of the viscosity of water, taken as unity at the temperature of the experiment.

Section A.—Changes during dialysis. Table I contains the results of these experiments.

TABLE I

Days of dialysis			Cat. speed $\times 10^5$	Sp. conductivity $\times 10^6$	F. V. with NH_4Cl	Relative Viscosity
0	..	..	13 00	998100 0	10·80	1·009
3	..	..	24·68	135330·0	9·90	0·968
5	..	..	33 70	3813·0	6·90	0·960
7	.	..	44·15	870·2	1 20	0 956
9	..	..	60 30	545·4	0 45	0·967
12	..	..	52·85	365·4	0·15	0·973
16	..	..	41·20	153·2	0·09	0·989
21	..	..	34·40	111·9	0·08	1·089
24	..	..	26·30	98·7	0·07	Highly viscous

With the progress of dialysis the cat. speed first increases and then decreases, while the conductivity and stability as determined by F. V. with NH_4Cl continuously decrease as in the case of $Fe(OH)_4$ [Desai and Borkar, *Trans. Faraday Soc.*, 1933, *29*, 1269], $Th(OH)_4$ [Desai and Desai, *Ibid*, 1933, *30*, 265], prussian blue [Mankodi, Barve and Desai, *Proc. Indian Acad. Sci.*, 1936, *4*, 480], V_2O_5 [Desai, Barve and Paranjpe, *Proc. R. S. E.*, 1939, *59*, 30] and zinc ferrocyanide investigated by Desai and co-workers. The viscosity first decreases and then increases with the progress of dialysis (Table I).

In the present instance $H^{\cdot}$, $Ce^{\cdots}$, and $Ce^{\cdots\cdot}$ are probably the preferentially adsorbed ions, which are responsible for the +ve charge on the colloid particles, and it will appear from a summary of the results given in Table III of Section C that on adding small increasing amounts of HCl and $CeCl_3$, the cat. speed first increases and then decreases. The changes in cat. speed during dialysis of ceric hydroxide can therefore be explained in the same manner as in the case of the colloidal solutions mentioned above [Desai and Barve, *Trans. Nat. Inst. Sci. (India)*, 1939, *2*, 39]. The changes in conductivity and stability can also be explained similarly.

It will appear that the view of Dhar and co-workers [*J. Indian Chem. Soc.*, 1932, *9*, 315, 441, 455 ; also see other papers referred to in these papers] that the smaller the charge, the greater the viscosity and vice versa is not completely supported by these results as the maximum in cat. speed and the minimum in viscosity have not occurred at the same stage of dialysis. The view of Smoluchowski [*Koll. Z.*, 1916, *18*, 194] is also not supported. While discussing the viscosity results one has to consider the various factors mentioned by Desai and co-workers [*Trans. Faraday Soc.*, 1933, *29*, 1269 ; *ibid*, 1933, *30*, 265 ; *Trans. Nat. Inst. Sci. (India)*, 1939, *2*, 39]. It should be mentioned here that Desai [*Kolloid chem. Beih*, 1928, *26*, 384] observed a continuous increase in viscosity with the progress of dialysis of this sol while the present results show an initial decrease in viscosity. This is due to the difference in the method of preparation of the sols. Desai prepared the sol by dialysing a solution of ceric ammonium nitrate and the particles of the sol so prepared are so highly hydrated that the influence of hydration on viscosity is predominant ; in the present case the sol is prepared by peptising ceric hydroxide with HCl and the particles of the sol are much less hydrated and hence viscosity also shows influence of other factors besides hydration.

Section B.—Changes during dilution of sols dialysed for different periods. The results of these experiments are given in Table II.

TABLE II

Days of Dialysis	DILUTION					
	1·00			1·25		
	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl
3	24·68	135330·0	9·90	25·10	10910·0	8·70
5	33·70	2813·0	6·90	35·31	2358·0	5·90
7	44·15	870·2	1·20	45·23	651·3	0·90
9	60·30	545·4	0·45	62·14	493·0	0·39
12	52·85	385·4	0·15	50·65	332·0	0·13
16	41·20	153·2	0·09	39·80	148·7	0·08
21	34·40	111·9	0·08	32·57	109·8	0·08

Days of Dialysis	DILUTION					
	1·50			2·00		
	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl
3	27·32	8305·0	7 00	28·91	6084·0	6·00
5	36·45	2150·0	5·10	38·15	1589·0	4·30
7	47·18	534·2	0·60	46·80	399·5	0·45
9	61·90	427·3	0 31	60·70	385·2	0·25
12	48·73	304·5	0·11	47·10	268·1	0·08
16	37·54	141·0	0·07	34·41	138·6	0·07
21	30·15	107·5	0·07	28·77	104·9	0·06

TABLE II—*contd.*

Days of Dialysis	DILUTION					
	3·00			5·00		
	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl	Cat. speed ×10⁵	Sp. conductivity ×10⁶	F. V. with NH_4Cl
3	29·10	3514·0	4·90	26·52	2358·0	3·20
5	36·90	1108·0	3·90	34·87	689·5	3·10
7	45·34	318·7	0·38	44·71	276·3	0·33
9	58·21	298·7	0·20	55·37	244·3	0·17
12	44·90	224·2	0·07	42·28	187·6	0·05
16	32·38	131·0	0·06	31·00	128·4	0·05
21	25·40	102·9	0·06	24·10	99·8	0·05

It will appear from the results given in Table II that in the case of sols dialysed for 3, 5, 7 and 9 days, the cat. speed first increases and then decreases on dilution, while for sols dialysed for longer periods the cat. speed continuously decreases. It is seen that the maximum cat. speed during dialysis has occurred between 8 and 12 days. The present results therefore completely support the previous results obtained with $Fe(OH)_3$, $Th(OH)_4$, prussian blue and zinc ferrocyanide sols and can be explained in the same manner [Desai and Barve, *Trans. Nat. Inst. Sci. (India)*, 1939, 2, 39]. The analogy between the processes of dilution and dialysis advanced in our papers [Desai and Borkar, *Trans. Faraday Soc.*, 1933, 29, 1269 ; Desai and Barve, *Trans. Nat. Inst. Sci. (India)*, 1939, 2, 39] would lead one to expect that the maximum value of cat. speed should occur at smaller and smaller dilutions with the progress of dialysis. The sols mentioned above showed a tendency to this effect. In the present case this effect is shown very clearly as for sols dialysed for 3, 5, 7 and 9 days the maximum cat. speed has occurred at dilutions 3, 2, 1·5 and 1·25 respectively.

The conductivity and stability as determined by F. V. with NH_4Cl continuously decrease on dilution of all the samples of the sol as in the case of zinc ferrocyanide sol and the present results can be explained in a similar manner [Vora, Barve and Desai, *Proc. Indian Acad. Sci.*, 1941, 13, 100 ; Desai and Barve, *Trans. Nat. Inst. Sci. (India)*, 1939, 2, 39].

Section C.—Changes in cat. speed of sols (dialysed for different periods) with the addition of increasing amounts of electrolytes. A summary of these results is given in Table III.

TABLE III

Electrolyte	Initial cat. speed	Initial rise in cat. speed	Cat. speed at which coagulation begins	Concentration of electrolyte at which coagulation begins
KCl	24·68*	5·17	24·15	0·150
	41·20*	*Nil.*	32·10	0·050
$K_2C_2O_4$	24·68	*Nil.*	21·70	0·0066
	41·20	*Nil.*	36·70	0·0066
$MgCl_2$	24·68	4·02	25·13	0·050
	41·20	*Nil.*	33·12	0·025
$BaCl_2$	24·68	1·44	20·30	0·0135
	41·20	*Nil.*	34·30	0·0063
HCl	24·68	21·69		
	41·20	2·34	No coagulation could be observed.	
$CeCl_3$	20·73	26·37		
	36·27	2·88		

* The initial cat. speeds are different as sols dialysed for different periods were used for these experiments.

It will appear from the results that as in the case of the sols previously studied, the initial rise in the cat. speed is not noticed when small increasing amounts of electrolyte having bivalent coagulating ion ($K_2C_2O_4$ in this case) are added to the sol. In the case of electrolytes having univalent coagulating ions, the initial rise in the cat. speed is noticed in all the cases except for the long period dialysed sol with KCl, $MgCl_2$ and $BaCl_2$. It may be that with concentrations still smaller than those tried in these experiments the initial rise might have been noticed even with the long period dialysed sol with the electrolytes in question.

The range of the cat. speed within which coagulation begins with the various electrolytes varies from 20·30 with $BaCl_2$ to 36·70 with $K_2C_2O_4$. These results therefore do not support the conception of a critical potential put forward by Powis (Zeit. Physik. Chem., 1915, LXXXIX, 156) [cf. Desai and Barve, *Trans. Nat. Inst. Sci. (India),* 1939, 2, 39].

Section D.—Changes on ageing of sols dialysed for different periods. The results of these experiments are given in Table IV.

TABLE IV

Age in days	Sol dialysed for 3 days				Sol dialysed for 16 days			
	Cat. speed $\times 10^5$	Sp. conductivity $\times 10^4$	F. V. with NH_4Cl	Relative viscosity	Cat. speed $\times 10^5$	Sp. conductivity $\times 10^4$	F. V. with NH_4Cl	Relative viscosity
0 ..	24·68	135·3	9·90	0·9667	41·20	1·532	0·100	0·9895
30 ..	24 00	128·7	8·44	0·9787	41·00	1·329	0·095	0·9916
60 ..	22·87	124 6	7 63	0·9816	39 23	1 165	0·087	0·9958
80 ..	21·64	..	6·42	0·9970	37·65	..	0·073	0·9991
90 ..	21·17	120·5	4·31	1·0580	36·81	0·099	0·061	1·0660
105 ..	20·73	117·3	3·90	.	36·27	0·077	0·049	..

The cat. speed, conductivity and stability of both the short period as well as long period dialysed sols continuously decrease with age (Table IV) and the changes can be explained in the same manner as done before [Desai and Barve, *Trans. Nat. Inst. Sci. (India)*, 1939, **2**, 39].

The increase in the viscosity with age is considered to be mostly due to
(1) an increase in the hydration and
(2) aggregation of the colloid particles.

The sol coagulates on allowing it to stand for a long time.

Section E.—Changes on exposure to sunlight of sols dialysed for different periods. Table V contains the results of these experiments.

TABLE V

Exposure to sunlight in hours	Sol dialysed for 3 days				Sol dialysed for 16 days			
	Cat. speed $\times 10^5$	Sp. conductivity $\times 10^4$	F.V. with NH_4Cl	Relative viscosity	Cat. speed $\times 10^5$	Sp. conductivity $\times 10^4$	F. V. with NH_4Cl	Relative viscosity
0 ..	24·68	135·3	9·90	0·9667	41·20	1·532	0·100	0·9895
3 ..	23·89	131 4	8·10	0·9612	40·87	1·321	0·097	0·9834
5 .	22·56	126·8	7·83	0·9552	40·10	1·165	0·091	0·9756
7 ..	21·55	.	7·10	0·9507	39·53	..	0·084	0·9698
9 ...	19·87	120·5	6·40	0·9486	38·40	0·987	0·076	0·9624
13 ..	19·10	116·4	5·00	0·9421	37·10	0·961	0·069	0·9554
18 ..	..	111·3	..	..	36·75	0·923	0·061	0·9502

On exposing both the short period and long period dialysed sols to sunlight, the cat. speed, stability and conductivity decrease, and the changes can be attributed to factors similar to those postulated in the case of the other colloidal solutions investigated in this laboratory [Desai and Barve *Trans. Nat. Inst. Sci. (India)*, 1939, 2, 39].

The viscosity has also decreased during exposure of the sol to sunlight. This decrease is considered to be mainly due to a decrease in the degree of hydration of the colloidal particles. On long exposure the sol coagulates. It is also known that under the influence of β or γ rays from radium, the viscosity of the ceric hydroxide sol first decreases and then increases.

Summary

The changes in the cataphoretic speed (cat. speed), conductivity, stability and viscosity of colloidal ceric hydroxide under different conditions have been studied.

It is found that with the progress of dialysis, the cat. speed first increases and then decreases, the conductivity and stability continuously decrease and the viscosity first decreases and then increases.

On dilution the cat. speed first increases and then decreases for sols dialysed for periods shorter than the maximum in the cataphoretic speed-dialysis curve, and continuously decreases for sols dialysed for longer periods. The conductivity and stability continuously decrease on dilution of both the short period and long period dialysed sols.

The idea of critical potential is not supported.

The cat. speed, conductivity and stability decrease while the viscosity increases during ageing of both the short period and long period dialysed sols.

On exposing the different samples of the sol to sunlight, it is observed that the cat. speed, conductivity, stability and viscosity decrease.

The results generally support the conclusions arrived at in the previous papers of this series.

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DIPOLE MOMENT AND MOLECULAR STRUCTURE
PART I
Dipole moments of ethyl esters of phenyl substituted acetic, malonic and glutaric acids

By

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A STUDY of the dipole moments of many organic compounds has shown that the hydrocarbon-alkyl radicals have no electrical moment or only a small one. If an H atom of a hydrocarbon is replaced by any other radical or atom a moment is produced which is associated with and is characteristic of the substituent in question.

In many respects, the phenyl radical behaves differently from the alkyl radical. The effect of alkyl substituents on different polar substances has been widely studied. The present work was undertaken with a view to study the effect of a phenyl group on the dipole moments of ethyl esters of phenyl acetic, malonic and glutaric acids.

EXPERIMENTAL

Preparation of esters.—All the esters were prepared according to standard methods described in literature. In each case the crude ester was hydrolysed to the free acid and the acid on purification was re-esterified. The esters thus obtained had the physical properties summarised in Table I.

TABLE I

Ester	B.P.	Density	Refractive index at 30
Ethyl-Phenyl-acetate	225–228°C	1·0240	1·4935
Ethyl-Phenyl-methyl acetate	228–230°C	1·0020	1·4875
Ethyl-diphenyl-acetate	58°C m.p.	....	....
Diethyl-phenyl-malonate	170°C at 12 mm.	0·0903	1·4900
Diethyl-phenyl-methyl malonate	165°C ,, ,,	1·0675	1·4888
Diethyl-diphenyl-malonate	200°C at 15 mm.	1·4846	1·4855
Diethyl βphenyl glutarate	188°C at 12 mm.	1·0661	1·4906
Diethyl ββdiphenyl glutarate	235°C at 7 mm.	1·0979*	1·5335*
"	*At 33°c.		

The physical constants given in this table agree very well with the values given in literature.

DETERMINATION OF THE DIELECTRIC CONSTANTS OF THE SOLUTIONS

Solvent.—In all these experiments Merck's pure benzene, thiophene free, and distilled twice or thrice over sodium was used.

Temperature.—All measurements of density, refractive index and dielectric constant of solutions were made at 30°C.

Preparation of solutions.—A small quantity of the ester was weighed in a stoppered flask of known weight. Benzene was added to it and the flask was weighed again. From these weights mol fractions of solute (f_1) and that of solvent (f_2) were calculated.

Density of solution.—Density was determined in a 25c.c. density bottle fitted with a thermometer and a side capillary tube. The volume of the liquid in the capillary was adjusted to a certain level at the desired temperature and the bottle was weighed. All the weighings have been corrected for buoyancy.

MEASUREMENT OF DIELECTRIC CONSTANT

Apparatus.—Dielectric constants were measured by the resonance method at 100 meters wave length. The apparatus used was the same as described by Bhide and Bhide (J. Univ. Bom. 1938 Vol. VII, Part 3, 93). The experimental condenser was of the same type as described Bhide and Bhide. (J. Univ. Bombay. 1939, Vol. VIII, Part 3, 220).

Calculations.—The mol fraction of the solute (f_1) dielectric constant (e_{12}) and density (d_{12}) of the different solutions were determined. A linear relationship was found between (f_1) and (e_{12}) and (f_1) and (d_{12}). The following equations will, therefore, represent their relationship.

$$e_{12} = e_2 (1 + \propto f_1)$$
$$d_{12} = d_2 (1 + f_1)$$

where e_{12} is the dielectric constant of the solution and e_2 of the solvent and d_{12} is the density of the solution and d_2 that of the solvent and $\propto$ and β are constants. For the sake of accuracy $\propto$ and β were calculated by the method of least squares.

Hedestrand (loc. cit.) has further shown that knowing the values of these constants the polarization at infinite dilution can be calculated according to the formula.

$$P_1 \propto = A (M_1 - M_2 \beta) + C \times \propto \times C\ e_2$$

where A and C are constants relating to the solvent and M_1 is the mol. wt. of solute and M_2 that of solvent.

The following table gives the values of the constants from the Hedestrand's formula, polarisation at infinite dilution $(P_1 \propto)$ calculated using the above constants, electron polarization (P_E) and the dipole moment μ in debye units which was calculated according to the formula :—

$$\mu = 0·0128 \times 10^{-18} \sqrt{(P_1 \propto - P_E)\ T}$$

In order to test the accuracy of the apparatus and the method of calculation, the dipole moment of diethyl malonate was determined. It was found to be $2\cdot535 \times 10^{-18}$. Smyth and Walls (J. A. C. S. 1931, 527) give $2\cdot54 \times 10^{-18}$ as the value for dipole moment of diethyl malonate. The accuracy in the measurements of dipole moments is within one per cent.

TABLE II

Ester	$\propto$	β	$P_1 \propto$	P_x	$\ln \overset{\mu}{D}$ebye units
Ethyl-phenyl-acetate	1·9637	0·3175	113·48	46·477	1·82
Ethyl-phenyl-methyl acetate	1·8955	0·2505	117·759	51·132	1·818
Ethyl-diphenyl acetate	1·8311	0·6218	126·871	64·388	1·761
$\propto ' =$	0·001984	(for refractive index).			
Diethyl-phenyl malonate	3·7867	0·5605	192·876	62·576	2·543
Diethyl-phenyl-methyl malonate ..	3·7704	0·6341	195·148	67·563	2·52
Diethyl-diphenyl malonate	11·0156	0·3197	467·907	72·119	4·433
Diethyl β phenyl-glutarate	3·7206	0·6338	197·978	71·594	2·505
Diethyl $\beta\beta$ diphenyl-glutarate	3·6720	0·8897	215·66	96·70	2·43

DISCUSSION

If a phenyl group is more electro-negative in character the moment of ethyl-phenyl acetate should be greater than that of ethyl acetate and that of ethyl-phenyl-methyl acetate greater than that of ethyl propionate. The moments are tabulated below :—

TABLE III

Acetates

Esters						$\mu \times 10^{-18}$
Ethyl-acetate*	..	..	..	..	..	1·835
Ethyl-phenyl acetate	..	..	..	..	..	1·824
Ethyl-diphenyl acetate	.	..	..	..	..	1·78
Ethyl propionate*	.	..		..	.	1·793
Ethyl-phenyl-methyl acetate	..	..	..	..	..	1·818

*Table of Dipole moments (Trans. Faraday Soc. 1934 × Lix).

Malonates

Diethyl malonate**	..	..	.	..	..	2·54
Diethyl-phenyl malonate	..	..	..	..	..	2·52
Diethyl-diphenyl malonate	..	..	..	..	..	4·43
Diethyl-phenyl-methyl malonate	..	..	..	..	..	2·52

Glutarates

Diethyl glutarate**	..	..	..	.	..	2·41
Diethyl-phenyl glutarate	..	..	..	..	..	2·51
Diethyl-diphenyl glutarate	..	..	..	..		2·43

**Smyth and Walls (J.A.C.S. 1931, 537.)

It would be seen from the above table that the moment of ethyl phenyl acetate is not far different from that of ethyl acetate. The moment of ethyl phenyl-methyl-acetate, however, is slightly greater than that of ethyl propionate. The electro-negative character of the phenyl group points out that the moment of ethyl-diphenyl-acetate should be appreciably greater than that of ethyl acetate or ethyl phenyl-acetate, but the observed moment is less than that of ethyl phenyl acetate and ethyl acetate.

The moments of diethyl-phenyl-malonate and diethyl phenyl-methyl-malonate are the same as that of diethyl malonate. But it is expected that they should have moments nearly the same as that of diethyl dimethyl malonate. The observed moment of diethyl dimethyl malonate is $2·32 \times 10^{-18}$ while the theoretical moment for diethyl dimethyl malonate should be about 2·31 (unpublished work). Therefore, diethyl-phenyl-malonate and diethyl-phenyl-methyl-malonate should have moments round about $2·32 \times 10^{-18}$ due to valency deflection. But the higher moments show that there is a definite small inductive effect.

The moment of diethyl-diphenyl-malonate deserves some remark. The moment of this ester is $4·43 \times 10^{-18}$. This high moment value may be perhaps accounted for by a different configuration of the carbethoxyl group in this ester (cf. Eucken and Meyer Z. Physik. 1929, 397).

The moments of diethyl β phenyl-glutarate and diethyl β β diphenyl glutarate are nearly the same as that of diethyl glutarate which is expected from the values of ethyl-phenyl-acetate and ethyl acetate. This shows that the inductive effect of the phenyl group in these glutarates is negligible.

According to the current electronic theories a phenyl radical is more electro-negative (—I-effect) than an alkyl radical. The electro-negative character of a phenyl radical is seen in the dissociation constants of phenyl substituted acids given below :—

Acetic acid	$1·75 \times 10^{-5}$
Phenylacetic acid	$4·88 \times 10^{-5}$
Diphenyl acetic acid	$11·5 \times 10^{-5}$

The considerable difference in dissociation constants of the acids referred to here has been attributed to electro-negative (—I effect) character of the phenyl group. But there is practically no difference in the dipole moments of phenyl substituted esters as shown above. This shows that the inductive effect of the phenyl group is very small and negligible. It *should be noted that Jenkins (J. C. S. 1940, 1447) has attributed the difference in dissociation constants not to the inductive effect but to* different resonance structures in the acids. In esters which we have studied, there is bound to be less resonance than in the corresponding acids. This definitely points out that the inductive effect of phenyl group is negligible.

SUMMARY

The study of the moments of ethyl esters of phenyl substituted acetic, malonic and glutaric acids has shown that the effect of the phenyl group on the moments of acetates and glutarates is negligible but there is a definite small inductive effect of the phenyl group on the moments of phenyl substituted malonates.

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DIPOLE MOMENT AND MOLECULAR STRUCTURE PART II

Dipole moments of ethyl esters of p-substituted benzoic acids

By

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WHILE studying the dipole moments of some aliphatic dicarboxylic esters, it was necessary to know the angles which the moment of the carbethoxy group makes with the C–C line. Hence with a view to determine this angle, the study of the dipole moments of ethyl esters of p-substituted benzoic acids was undertaken.

The moments of p-substituted compounds, such as p-dichloro-benzene, p-dinitro-benzene, p-diiodo-benzene, etc., have been found to be zero. This clearly indicates that the valencies of the carbon atom in the benzene ring act in the plane of the ring. In the para-substituted benzoic esters the carbethoxy group and the p-substituent are far away from one another and therefore the inductive effect of the carbethoxy group on the p-substituent may be assumed to be negligible (Frank J. C. S. 1936, 1324). Comber and Partington (J. C. S. 1938, 1444) have measured the moments of p-substituted benzaldehydes and measured the angle which the moment of the aldehyde group makes with the C–C line. Brooks and Hobbs (J. A. C. S. 1940, 2851) have studied the moments of p-substituted benzoic acids and have shown that the moment of the carbethoxy group makes an angle of 74–76° with the C–C line.

The inductive effect of substituents on the phenyl group has been discussed by Frank (loc. cit.) and Sutton (J. C. S. 1933, 409). Their calculations indicate a large induced moment in the phenyl group due to substituents. If we compare the moment of ethyl acetate (1·83) and ethyl benzoate (1·93), the apparent induced moment in the phenyl group due to the presence of the carbethoxy group appears to be small and as we intend to apply the results to the aliphatic esters we have not taken into consideration this induced moment in our calculations.

EXPERIMENTAL

Preparation of esters.—The esters were prepared by the usual Fischer-Speier's method from the pure crystallized acids which were either bought or prepared according to standard methods described in literature. The

physical properties of the esters studied have been summarised in the following table :—

TABLE I

Ester	B. P.	Density at 30°C	Refractive index
Ethyl Benzoate	212°C	1·4227	1·50133
„ p-Chloro benzoate	238°C	1·17617	1·51313
„ p-Bromo benzoate	260°C	1·40316	1·51217
„ p-Nitro benzoate	57°C m.p.	....	....
„ p-Amino benzoate	92°C m.p.	....	....

The physical constants given in this table agree very well with the values given in literature.

Determination and calculations of Dipole moments.—The apparatus and the method of calculation have been described in Part I (see the previous paper). The following table gives the values of the constants $\propto$ and β of Hedestrand's Formula (Z. Physik, Chem. 1929, *B2*, 428) and the polarization at infinite dilution ($P_1 \propto$) the electron polarization (P_E) and the dipole moment (μ) in debye units :—

TABLE II

Esters	$\propto$	β	$P_1 \propto$	P_E	μ	Previous value of μ if any
						At 20 :
Ethyl Benzoate	2·2453	0·3314	117·73	42·44	1·93	1·92*
Ethyl p-chloro Benzoate .	3·0299	0·6297	147·89	47·158	2·24	2·0†
Ethyl p-bromo Benzoate ..	3·0527	1·1257	156·96	48·98	2·31	..
Ethyl p-nitro Benzoate ..	9·8725	0·7824	377·12	46·45	4·05	..
	$\propto' = 0$·04471 (for refraction).					
Ethyl p-amino Benzoate ..	7·260	0·5271	285·92	48·43	3·41	..
	$\propto' = $ for refraction $= 0$·204.					

*Donle (Z. Physik Chem. 1931, *B14*, 362).
†Bergmann (Z. Physik Chem 1931, *B15*, 85).

(*cf.* Trans. Faraday Soc. 1934, Table of Dipole Moments).

(Our values for the moments of ethyl benzoate and ethyl p-chloro-benzoate agree with the previously determined values.)

DISCUSSION

The approximate angle that the moment of the carbethoxy group makes with the C–C line has been calculated according to the following equation :—

$$\text{Cos } \omega = \frac{\mu^2 - m_1{}^2 - m_2{}^2}{2m_1 \, m_2}$$

Where μ is the resultant moment

$m_1 =$ is the moment of the ester group as taken from the moment of ethyl benzoate

$m_2 =$ is the moment of the p-substituent, the value of which is taken from the Table of Dipole Moments (Trans. Faraday Soc. 1934).
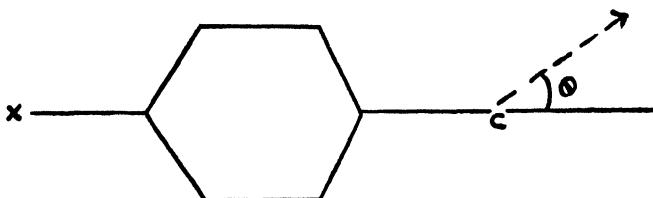
$$X = C\ell, \; \text{or} \; B\lambda, \; \text{or} \; NO_2 \; \text{or} \; NH_2 \qquad\qquad FIG.I$$

The following table gives the values of μ, m_1, m_2 and the angle of ω obtained according to the above equation :—

TABLE III

Substituent			μ	m_1	m_2	ω
p-chloro	..	..	2·24	1·93	1·56	76°
p-bromo	..	..	2·31	1·93	1·58	82°
p-nitro	..	..	4·045	1·93	3·942	79°
p-amino	..	..	3·41	1·93	1·53	....

It will be seen that the value of the angle—the angle that the moment of the carbethoxy group makes with the C–C line—is 76°, 82°, 79° for p-chloro, p-bromo and p-nitro compounds respectively.

The average angle, therefore, is 79 degrees. It should be noted that recently Brooks and Hobbs (loc. cit.) have found the average value of this angle to be 76° in case of p-substituted benzoic acids.

Ethyl p-chloro benzoate has a lower moment than that of ethyl p-bromo benzoate, the reverse of what might be expected. A similar lower moment for p-chloro benzoic acid as compared with that of p-bromo benzoic acid has been observed by Brooks and Hobbs (loc. cit.).

The case of ethyl p-amino benzoate appears to be peculiar. The direction of the moments of the amino group and the carbethoxy group are parallel and unidirectional.

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STUDIES* ON THE DEPOLYMERISATION OF ACONITIC ACID: [CH.COOH]₃

By

I. D. SHIVA RAO

IN a recent publication, A. Miolati, of the Royal University of Padua, with the collaboration of the author, had mentioned various facts, concerning the formation of free radicals, [Contributi alla Conoscenza dei Composti Organici, R. A. d'Italia, Memorie delle Classe di Scienze Fisiche, Matematiche e Naturali, VIII, 5, pp. 215-241, 1937], and of the formation of complex organic compounds, from the thus formed more simple free radicals. These facts have not only made clearer our ideas in regard to the energy values of the four valencies of the carbon atom, but also have rendered very plausible the existence of the labile molecules. These molecules may be called the elementary constituents of many compounds, known and studied in Organic Chemistry. The complex molecules are formed from the labile ones, by a simple process of polymerisation, which would represent a stabilising process of the latter, just as we note in the case of many lower members of the homologous series.

Some of these labile molecules are:

$$CH_2.COOH\ ;\ CH_3.C\ [OH].CH_3\ ;\ C_6H_5.CH\ [OH]\ ;$$
$$CH.COOH\ ;\ CH.OH.COOH.$$
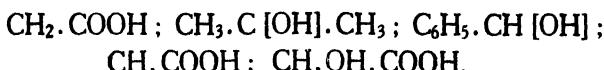
Succinic acid would be a dimer of the labile molecule $CH_2.COOH$. We may, therefore, not exclude the possibility of a dissociation equilibrium of the type:

$$[CH_2.COOH]_2 \rightleftarrows 2CH_2.COOH$$
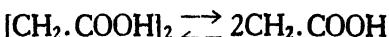
though it may probably be totally displaced towards the left, i.e., to the ordinary succinic acid. This apparently renders it impossible to detect analytically the presence of the molecule $CH.COOH$. Such an equilibrium, incidentally it may be mentioned, is not much different from that of acetic acid:

$$[CH_3.COOH]_2 \rightleftarrows 2CH_3.COOH$$
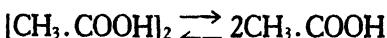
The polymerised molecules of acetic acid exist also in the state of vapour, as can be verified by the vapour density determination of acetic acid at low temperatures.

In the case of succinic acid, A. Miolati suggested the possibility of detecting the $CH_2.COOH$ molecule, when it is adsorbed on a solid where surface forces play a great part, just as diatomic hydrogen and oxygen may be in equilibrium with the monoatomic form when they are adsorbed at a solid surface.

---

* The Author regrets that the polarograms sent to Italy, for final confirmative remarks, just before Italy entered the war, could not be had back for publication. The explanations and calculations are, however, sufficiently clear without them.

The same may be said with regard to the molecule $CH.COOH$, which by auto-association would first give fumaric [or maleic] acid, and on further association aconitic acid :

$$2CH.COOH \rightleftarrows [CH.COOH]_2 \text{ and } 3CH.COOH \rightleftarrows [CH.COOH]_3$$
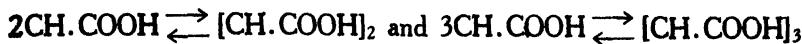
An experimental proof of the existence of the labile molecules $CH.COOH$ and $CH_2.COOH$ was given by Dr. Semerano [*ibid*, pp. 243–253]. By a discussion of the results obtained in the reduction of maleic, fumaric and aconitic acids at a cathode in the form of mercury drops, he has shown :

(*i*) that the reduction of aconitic acid is a trivalent process ; and

(*ii*) that among the products of reduction succinic acid is present.

This indicates the presence of a liable molecule $CH.COOH$ at the electrode, by the hydrogenation of which $CH_2.COOH$ would be formed, and finally by polymerisation, succinic acid.

On a further particularised study of the polarograms obtained by electrolysing maleic, fumaric and aconitic acids, under various experimental conditions he has confirmed the previous assertions. In the inter-phase Hg/H_2O an acid, weaker than, but common to, the three dissolved acids was present. The fumaric and maleic acids were, therefore, the dimers, and aconitic acid, the trimer, of the same labile acid $CH.COOH$. Dr. Semerano has also been able to calculate the dissociation constant of the acid $CH.COOH$, and the extent of polymerisation into the three acids, maleic, fumaric and aconitic. His conclusion is that in the inter-phase Hg/H_2O maleic acid is more dissociated than the other two.

Ordinary aconitic acid, according to J. F. Thorpe and H. Rogerson [J. Chem. Soc., Lond., 1906, 89, 631] is symmetrically constituted with free valencies at the $\propto$ and the γ carbon atoms :
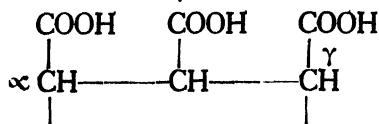
According to N Bland and J. F. Thorpe [*ibid*, 1912, 101, 1490], however, there is besides a labile form of aconitic acid, melting point 173°C, to which Thorpe assigned the formula of an ordinary propen- $\propto$ -β-γ-tricarbonic acid :
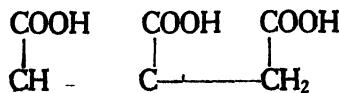
This is prepared by the hydrogenation of its anhydride, likewise, labile, the so-called hydroxy-anhydrous acid [m. p. 135°C], which in its turn is prepared by long heating of the ordinary aconitic acid, in a chloroformic solution, either with acetic anhydride [P. F. Varkade Rec. Trav. Chim. Pays-Bas, 1921, 40, 381], or with acetyl chloride, absolutely free from phosphorous trichloride [N. Bland and J. F. Thorpe, loc. cit.].

P. Malachowski and N. Maslowski, [B. 1928, 61, 2521], have found out, that the relation between these two acids and the products of their dehydration cannot be correctly represented, accepting the conclusion of Thorpe, but only when we admit what Feist had admitted in the case of glutaconic acid [A. 1909, 370, 41], namely that the two acids are between themselves in the relationship of cis- and trans- isomers. The ordinary aconitic acid [m.p. 194°–195°C] would be the more stable trans-variety :

$$
\begin{array}{ccc}
H & & COOH \\
\diagdown & & \diagup \\
C & = & C \\
\diagup & & \diagdown \\
HOOC & & CH_2 \cdot COOH
\end{array}
$$

The cis- form, corresponding to the labile, viz.,

$$
\begin{array}{ccc}
HOOC & & COOH \\
\diagdown & & \diagup \\
C & = & C \\
\diagup & & \diagdown \\
H & & CH_2 \cdot COOH
\end{array}
$$
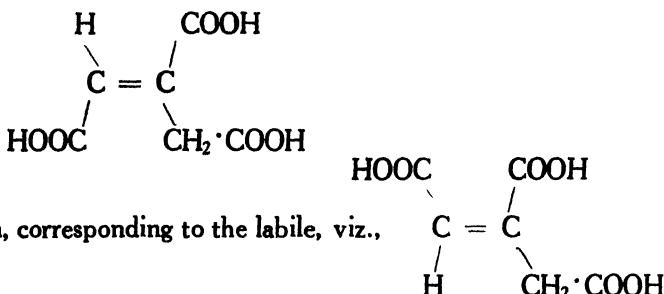
was prepared by Malachowski and Maslowski, hydrolising the so-called "acid-anhydride" [m.p. 78°C], the other anhydride of aconitic acid, which in its turn is prepared from ordinary aconitic acid and commercial acetyl chloride, in a chloroform solution, without heating ; or even by simple heating of the ordinary aconitic acid at 140°C under a strongly reduced pressure [R. Auschutz and W. Bertram, B. 1904, 37, 3967].

The cis- form fuses at 125°C and easily gets transformed into the trans-either on fusing or by slightly heating the water solution. It can easily be brominated, forming a bromide different from that derived from the trans- variety. Dehydrating agents transform it into the anhydrous acid, which should therefore be considered as its anhydride.

According to Malachowski and Maslowski, the labile form suggested by Thorpe does not exist. On hydrating the hydroxy-anhydride following the method of Bland and Thorpe, with sodium or potassium hydroxide, they obtained the simple ordinary aconitic acid [m.p. 182°–183°C] as a 20 per cent. yield ! [Note : Pure aconitic acid, crystallised, first from strong hydrochloric acid, and then from distilled water has melting point 194°C]. On simple water hydrolysis they obtained the same acid [m.p. 184·5-186°C] as a 42 per cent. yield, and another fraction, approximately 30 per cent., with the melting point 179–189°C. Even on hydrolysis with concentrated hydrochloric acid they obtained the ordinary acid [m.p. 179°C]. The hydrolysis of the hydroxy-anhydride, therefore, gives the trans-aconitic acid, rather in the impure state, and hence with a melting point approximately 12°C. lower than the purified sample. This anhydride must be from the trans-acid.

The symmetric constitution [cfr. p. of this article] suggested by Thorpe and Rogerson, therefore, does not exist. The identity between the ∝ and γ methyl derivatives of aconitic acid [J. F. Thorpe and H. Rogerson, above] must be explained by a secondary transformation of the less stable form under the chosen experimental conditions. Later R. Malachowski,

M. Giedroyc and Z. Jerzmanowska [B. 1928, 61, 2525], studied the conditions of formation and the constitutions of the cis- and trans- anhydrides of aconitic acid :
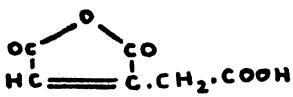
Cis-anhydride [m.p. 74°C]   Trans-anhydride [m.p. 134–135°C]

It has further been shown, by A. Miolati, G. Semerano and the author [loc. cit. p. 216] that ordinary aconitic acid may be considered as a trimer of the labile acid CH.COOH. To confirm such a view, a series of experiments were done, to see if aconitic acid can be depolymerised under certain conditions, and made to get transformed into maleic, or more probably into the stabler form fumaric acid, which last as has been already shown by us should be considered as a dimer of the labile acid CH.COOH [*ibid*].

EXPERIMENTAL

Two series of experiments were conducted : (1) Aconitic acid was fused under various conditions, and fumaric acid was looked for in the products of fusion. (2) A solution of aconitic acid was agitated for a sufficient time with activated carbon. This latter was done, basing ourselves, on the observation made by us [loc. cit.], that on a mercury surface, the three acids, aconitic, maleic and fumaric are notably dissociated into labile molecules CH.COOH. By adsorption, therefore, there was the possibility, that the labile molecules CH.COOH get polymerised into the dimer maleic acid, or more probably into the stabler form fumaric acid.

Heating of aconitic acid

A pure sample of aconitic acid was obtained by the method suggested by G. Semerano [loc. cit.]. The sample supplied by Shering-Kahlbaum was repeatedly precipitated from a water solution by means of gaseous hydrogen chloride, and dried in vacuum over calcium chloride and potassium hydroxide.

Approximately 0·0050 grams each of this purified sample, was enclosed either alone or with suitable catalysts in small " melting point " tubes, and these tubes were heated at various temperatures, for different periods of time. The small empty space in the tubes gathered all the gaseous products formed and established a very high pressure of carbon dioxide, so that the decomposition of aconitic acid into water, carbon dioxide and itaconic anhydride was reduced to a minimum. After a short time the

substance in the tube melted into a more or less brown liquid and gathered at the bottom of the tube which was held vertical. On cooling the melted liquid solidified at the bottom, so that when the tubes were later opened for analysis the gaseous products escaped with extreme violence, but the solid remained intact at the bottom of the tube.

In the case of a few of these tubes, the solid substance was discarded, the tubes being opened under mercury in the Bone-Newitt gas analysing apparatus. The gaseous product proved exclusively to be carbon dioxide. In the remaining cases, however, the solid at the bottom of the tubes was analysed.

Fumaric acid was looked for by the polarographic method, as the yield was expected to be so small that no other method could give satisfactory results.

To settle the best conditions for the polarographic analysis, solutions with known concentration of : 1° *Fumaric acid in N. Hydrochloric acid ;* 2° Calcium fumarate in 0˙4832 N. ammonium chloride solution ; and 3° Lithium fumarate in 0˙100 N. Lithium chloride solution were first electrolysed [G. Semerano and the Author, Mikrochemie, 1937, Band 23, pp. 10–11], and their polarograms obtained.

The heated samples were separately crushed in a mortar, and the soluble part was dissolved in one c.c. of distilled water. This solution was neutralised with $3˙73 \times 10^{2}$ N. Ca $[OH]_2$, using phenolphthalein as indicator, and then divided into two equal parts. To one part the calculated quantity of a strong solution of lithium chloride was added so that the final solution had the same concentration in lithium chloride as that in the preliminary experiments, viz., 10^{-1} N. The polarograms of these solutions were obtained with the usual polarographic disposition, using the galvano-meter at 1/1000, 1/500 and 1/100 of its maximum sensibility, which was 10^{-9} amps./mm. m. The experiments were conducted at 28°C without eliminating the oxygen present in the solution, as the reduction potentials of the anions in question, fumaric and aconitic, were considerably negative. The other part was also similarly experimented upon, except that ammonium chloride was used instead of lithium chloride. The strength of the ammonium chloride, the indifferent solution, was kept at 0˙4832N in the final stage, just as in the preliminary experiments.

To help the study of the polarograms thus obtained, further curves of " current-potential " were obtained of 1° Neutral calcium aconitate in ammonium chloride, and 2° Neutral lithium aconitate in lithium chloride, having the same concentration of the indifferent solution. The results calculated from the curves obtained with various known concentrations of

calcium aconitate in 0·4832 N. ammonium chloride are shown in the following table :

TABLE 1

Solution of Calcium Aconitate in Ammonium Chloride 4·832 × 10^{-1} *N.*

Expt. No.	Concentration of the aconitate [moles/litre]	Intensity of the current of diffusion [in 10^{-7} amps.]		Reduction Potential calculated according to Semerano [for molar solution]
		Observed	Calculated for 10^{-4} mols.	
1	1·18 × 10^{-3}	29·9$_8$	2·54	−1·566 volts.
2	2·03 ,,	50 9$_6$	2·51	−1·564 volts.
3	2·66 ,,	68·6$_2$	2·58	−1 568 volts.
4	3·16 ,,	80 2$_5$	2·54	−1·568 volts.
5	4·57 ,,	116 5$_4$	2·55	−1·568 volts.
6	4 88 ,,	123·9$_6$	2·54	−1·568 volts.

The curves, besides showed a maximum similar to that shown by the curve of calcium fumarate.   The molar reduction potential of the fumarate, which is −1·44 volts [calculated from G. Semerano, loc. cit., p. 258, table I] is therefore, more positive than that of the aconitate,−1·57 volts.   To detect the presence of aconitic acid was thus possible by this method. In the case of lithium acconitate in lithium chloride, the curves obtained showed a potential of reduction very slightly different from that shown in the case of lithium fumarate in lithium chloride, so much so that a comparative study of the two sets of polarograms was almost impossible.

Again, experiments conducted with itaconic acid, which is formed by the elimination of carbon dioxide from aconitic acid, showed that neither itaconic acid in hydrochloric acid solution, nor calcium itaconate in ammonium chloride, nor still lithium itaconate in lithium chloride give diffusion curves. Only the potential of deposition of the H˙, or of the NH$_4^+$ or of the Li˙ ion˙ gets slightly rendered positive.   There was still a possibility that in the decomposition of aconitic acid, citraconic anhydride be formed from the itaconic anhydride. Citraconic anhydride was, therefore, studied polarographically.   The results from the curves, obtained only in the case of the citraconic anhydride in hydrochloric acid, N., and of the calcium citraconate in 0·4832 N. NH$_4$Cl solutions, are

given below : Lithium citraconate in lithium chloride did not give any diffusion curves.

TABLE 2a

Citraconic Anhydride in Normal Hydrochloric Acid

Expt. No.	Concentration of Citraconic anhydride [moles/litre]	Intensity of the current of diffusion [in 10^{-7} amps.]		Reduction potential calculated according to Semerano [for molar solution]
		Observed	Calculated for 10^{-4} mol. sol.	
1	$1·48 \times 10^{-3}$	92·79	6·29	—0·452 volts.
2	1·97 ,,	124·90	6·34	—0·453 volts.
3	2·63 ,,	167·5₂	6·37	—0·454 volts.
4	3·50 ,,	223·6₅	6·39	—0·453 volts.
5	4·67 ,,	294·21	6·30	—0·453 volts.

TABLE 2b

Calcium Citraconate in $0·4832$ N. Ammonium Chloride solution

Expt. No.	Concentration of Citraconic anhydride [moles/litre].	Intensity of the current of diffusion [in 10^{-7} amps.]		Reduction potential calculated according to Semerano [for molar solution].
		Observed.	Calculated for 10^{-4} mol. sol.	
1	$3·45 \times 10^{-3}$	159·0₆	4·61	—1·416 volts.
2	3·70 ,,	170·9₄	4·62	—1·416 volts.
3	3·80 ,,	175·56	4·62	—1·410 volts.
4	4·22 ,,	195·39	4·63	—1·399 volts.
5	5·43 ,,	250·87	4·62	—1·399 volts.

From these tables it is clear, that both in the acid and in the ammonium chloride solution, the reduction potential of the citraconate radical is not much different from that of fumaric acid in the same solutions [—0·438 and— 1·44 volts, cfr. Semerano, loc. cit.].   In compensation, as already

said, the polarograms show that while solutions of lithium fumarate in lithium chloride do give diffusion curves, those of lithium citraconate in lithium chloride do not give such curves, so that the comparison of these curves may serve to differentiate between them.

From these conclusions, and studying the curves obtained from the heated samples of aconitic acid, it was deduced that, although a partial transformation of the itaconic anhydride formed into the citraconic anhydride cannot be excluded, the waves in the curves obtained clearly indicated the presence of fumaric acid, 1° because, the molar potential of reduction corresponded exactly to that of fumaric acid, and 2° because, when the quantity of fumaric acid was in sufficient excess, curves could be got even in lithium chloride, in which indifferent solution citraconic anhydride does not give diffusion curves. The following table gives the results of the determinations. While calculating the percentage of aconitic acid transformed into the fumaric acid, account was taken of the fact that from two molecules of aconitic acid, three molecules of fumaric acid would be formed :—

TABLE 3

Expt. No.	Wt. in grams of aconitic acid heated	Catalyst	Temperature	Time	Percentage of fumaric acid formed
1	0·0060	*Nil*	160°C	6h. 15m.	3·4
2	0·0048	*Nil*	149°C	2h. 20m.	2·8
3	0·0052	Manganese Orthophosphate	211°C	2h.	15·2
4	0·0054	Manganese Dioxide ..	170°C	2h.	5·7
5	0·0050	Allumina	133°C	1h. 30m.	3·8
6	0·0050	Allumina	167°C	1h. 30m.	16·1
7	0·0049	Manganese Orthophosphate	133°C	1h. 30m.	8·7
8	0·0048	Allumina	201°C	1h. 45m.	10·0

It can thus be asserted that in fusing aconitic acid, a notable quantity of it gets transformed into fumaric acid.

A further set of experiments were then made to study the manner in which the itaconic anhydride, the principal product of the decomposition, is formed. As we can consider aconitic acid as [CH. COOH]₃, it was thought that the formation of the itaconic anhydride may be according to the following mechanism. The labile molecule CH. COOH, the first product of decomposition of aconitic acid,

$$[CH. COOH]_3 \rightarrow [CH. COOH]_2 + CH. COOH,$$

may decompose thermally in an analogous way to acetic acid :

$$CH_3. COOH \rightarrow CH_4 + CO_2$$

$$CH. COOH \rightarrow CH_2: + CO_2$$
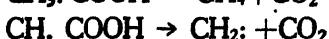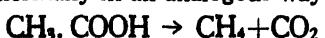
The labile molecule CH_2 : fixed by the dimer [CH. COOH]$_2$ would then give itaconic acid, CH_2. [CH. COOH]$_2$, from which by consecutive dehydration, the itaconic anhydride would be formed. If this hypothesis is plausible, there is a certain possibility, that the labile molecule CH_2: so produced, instead of fixing itself on to the dimer [CH. COOH]$_2$ may get polymerised to ethylene, C_2H_4.

The existence of the labile molecule CH_2 : was long admitted by G. Orlow, [B. 42, 894], to interpret the formation of C_2H_4 from carbon monoxide and hydrogen. The carbon monoxide first gets reduced to CH_2 : by hydrogen, and by the succeeding condensation, ethylene would be formed :

$$CO + 2H_2 \rightarrow CH_2 : + H_2O$$

$$2CH_2 : \rightarrow C_2H_4$$
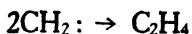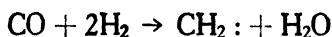
L. S. Kassel, from his study of CH_4, has suggested that CH_2 : is chemically rather inactive. From more recent researches, however, F. O. Rice and A. L. Glazebrook have put to doubt, not only this inactivity, but also the part played by CH_2 : in the pyrolisis of CH_4. Norrish has shown the probable formation of CH_2 : in the photodecomposition of diazomethane. It is even admitted that the labile molecule CH_2 : is even of greater importance in the decomposition and synthesis of organic compounds, than CH_3. or C_2H_5.

In the experiments that follow, the attention was more directed to the finding of C_2H_4 in the gaseous products of the thermal decomposition of aconitic acid.
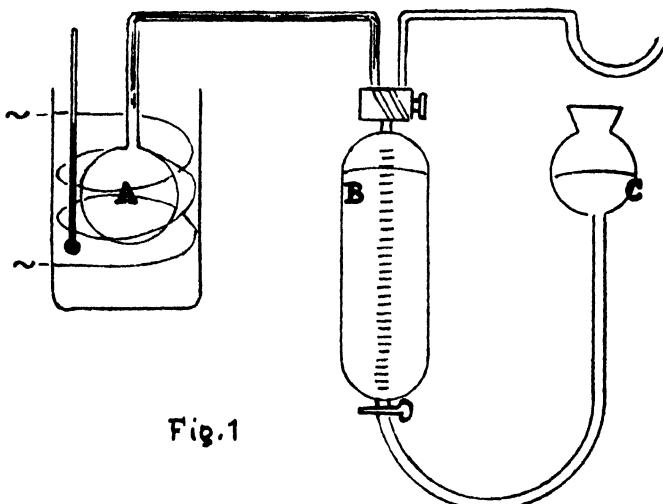
Fig. 1

The first experiment was done by heating 2·136 gms. of aconitic acid in the bulb A of the apparatus here shown. The gas evolved was collected

over mercury in the burette B. The experiment was conducted at atmospheric pressure, by adjusting the position of the bulb C. The vessel A was connected to the burette B by means of a capillary tube. A vacuum was produced in the apparatus by means of an oil suction pump, which displaced also all the air occluded in the aconitic acid itself. The vessel A, after being exhausted was introduced into an electric furnace, kept at a constant temperature of $178°C$ [± 0.5] for seven and a half hours. Together with the times and corresponding temperatures, the approximate volumes of the gas evolved was also measured in the graduated burette B. In the beginning the evolution of the gas was very slow. After 45 minutes' heating, it accelerated reaching a maximum rate after about two hours' heating, and slowed down again, after half an hour's rapid evolution. After about seven and a half hours the evolution practically stopped.

The volume of gas evolved corresponded almost to the quantity of CO_2 that should be obtained in the transformation of aconitic acid into itaconic acid :

$$CH.COOH \qquad\qquad CH_2$$
$$\|\qquad\qquad\qquad\qquad \|$$
$$C.COOH \quad \rightarrow \quad CO_2 + C.COOH$$
$$|\qquad\qquad\qquad\qquad |$$
$$CH_2.COOH \qquad\qquad CH_2COOH$$
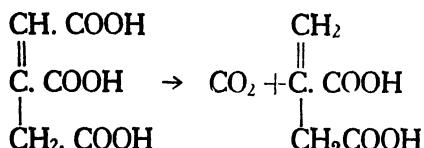
Analysis of the gas evolved done at $28°C$ gave 99.8 per cent. of carbon dioxide.

It was clear thus, that when the gas was made to evolve slowly from aconitic acid the product was exclusively CO_2. But a doubt remained that probably the molecules of CH_2 : had too much time to get compelled to associate themselves with the molecules of $[CH.COOH]_2$, thus not being able to form the expected dimer C_2H_4. The apparatus was, therefore, modified to have rapid development of the gas.
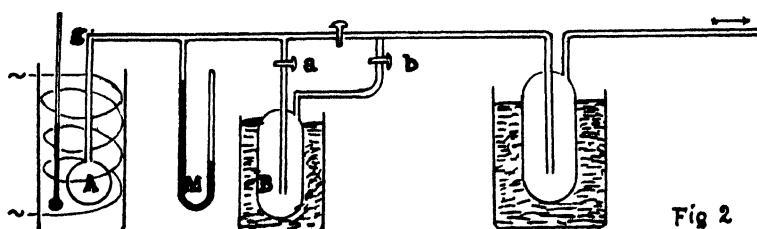
Fig 2

1.5666 gms. of aconitic acid were weighed out in the bulb A. The manometer M registered the pressure in the apparatus during the experiment. The recipient B in which the gaseous products were collected, was surrounded by liquid air in a Dewar's bottle. Another recipient also surrounded by liquid air, trapped any water vapour that would have got into the apparatus from the water suction pump, used to exhaust the apparatus of all the air.

With the taps a and b closed, the suction pump was set. When there was practically a vacuum registered by the manometer, these taps were gradually opened so that all the air in the whole apparatus and that occluded in the acid was practically sucked out, care being taken that none of the weighed acid in the vessel A was sucked through. A high vacuum was not maintained in the apparatus as it was known that below a few millimeters of pressure, at temperatures higher than 140°C both itaconic and aconitic acids sublime without undergoing any alteration [E. Mohr, B. 28, 2588]. When the manometer M registered a constant pressure, the vessel A was introduced into an electric furnace at a constant temperature of 160°C [$\pm$ 0·5°] and was there heated for two hours and a half. The gas condensed in the vessel B was evaporated into the analysing apparatus, and on analysis gave 97·1 per cent. of CO_2 and 2·9 per cent. of ethylene. This latter was estimated according to the method used by the author for similar estimations [Jour. of the Univ. of Bombay, Nov. 1940, vol. IX, part 3, p. 96]. Besides these gaseous products, in the bend g of the apparatus condensed a considerable quantity of a liquid B. P. 100°C—evidently water—which is produced while heating aconitic acid at above 140°C in a vacuum [R. Auschutz and W. Bertram, loc. cit.]. The formation of the acid anhydride was confirmed by determining the melting point of the residue left in the vessel A.

The experiment was repeated a third time both with the intention of analysing the solid residue and the liquid products—for the most part water—and also, because of the fact that at the temperature of liquid air the vapour pressure of ethylene is already sufficiently high, so that most of the ethylene might have been sucked out during the previous experiment. To avoid this, the decomposition of the acid was done in a vacuum, but instead of continuously sucking out the gaseous products, these were taken out at intervals, so that the apparatus had always more or less the pressure of the water vapour evolved during the decomposition.
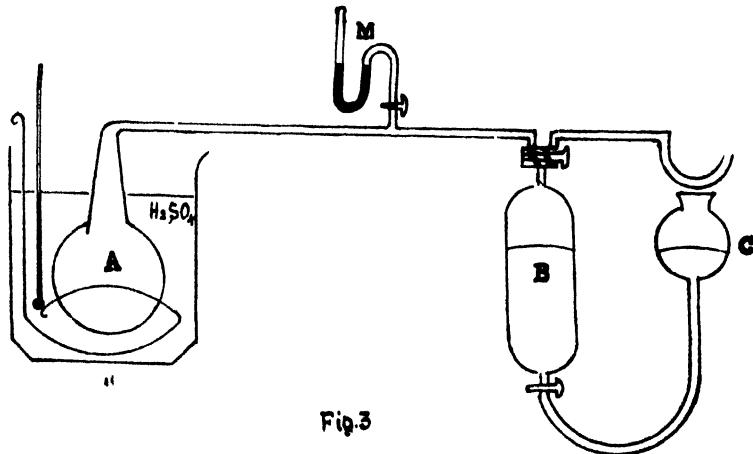
Fig.3

The apparatus was slightly modified as in the figure. Instead of the electric furnace, a concentrated sulphuric acid bath was used, so that the whole process of decomposition could be watched during the experiment. The manometer M introduced between the vessel A and the recipient B indicated the pressure in the apparatus. The joints were all soldered together so that there might be no leakage.

2·0056 gm. of aconitic acid was weighed in the vessel A and all the air, even that occluded in the acid was pumped out. Having obtained a vacuum in the apparatus the vessel A was introduced into the sulphuric acid bath maintained at the constant temperature of 158°C [± 0·5], and kept there for two hours. After an hour's heating a rapid bubbling of the gas was noticed in the vessel A, though no appreciable change in the pressure could be observed. It was evident that the gas evolved at this stage was mostly steam, which was condensing copiously at the cooler parts of the apparatus. The gas which was repeatedly transferred from the burette B, to avoid any considerable pressure inside the apparatus, was analysed in the usual manner and gave the following result : $CO_2 \rightarrow 97·03$ per cent. $C_2H_4 \rightarrow 2·97$ per cent.

The residue in the vessel A weighed 1·7566 gms. This was dissolved in 25 cc. of distilled water. The greater part dissolved easily. The insoluble part was kept suspended in water for about 15 hours and then filtered. The still insoluble residue was repeatedly washed with about 2 cc. of distilled water at the boiling temperature. Still a small black portion remained undissolved. From the above two solutions polarograms were obtained first in acid solution and then in neutral solution. That from the acid solution showed the excessive presence of aconitic acid which was produced from the anhydride on being dissolved. That from lithium chloride showed an yield of 0·62 per cent. of fumaric acid produced from the aconitic acid, during the heating.

The following mechanism of the decomposition of aconitic acid was, therefore, plausible :

1. $[CH. COOH]_3 \rightarrow CH. COOH + [CH. COOH]_2$ [fumaric acid]
2. $CH. COOH \rightarrow CH_2 : \quad + CO_2$
   $2CH_2 : \rightarrow C_2H_4$
3. $CH_2 : + [CH. COOH]_2 \rightarrow CH_2 . [CH.COOH]_2 \rightarrow CH_2 [CH.CO]_2.O + H_2O$
   $\qquad\qquad\qquad$ itaconic acid $\qquad$ itaconic anhydride

Simultaneously a couple of experiments were done to look for fumaric acid in the aconitic acid solution that was shaken with active carbon for a sufficiently long time. The probable reason for such a conclusion has been already given.

0·0145 gms. of aconitic acid were weighed out in a hard glass test-tube and dissolved in 5 cc. of distilled water. 0·11 gm. of activated carbon were then added to the solution, and the whole was kept in an agitator for six hours and forty minutes. The solution was then filtered from the carbon. 3 cc. of the resulting solution was neutralised with 0·22 cc. of

0·63 N. lithium hydroxide, and with the addition of 0·41 cc. of lithium chloride [0·884 N], the solution was rendered 0·1 N. in lithium chloride. With this solution in the cell the " current-tension " curve was obtained. The curve showed all the characteristics of the presence of fumaric acid, whether in regard to its shape, or in regard to the potential of reduction. There was not even the slightest indication of the presence of aconitic acid, so that it could be concluded that all the aconitic acid was transformed into the fumaric acid. The height of the wave was 550×10^{7} amps. The original aconitic acid solution was $1·64 \times 10^{-2}$ mol. Taking into account that the solution was diluted from 3 to 3·63 cc. (the strength reduces to $1·36 \times 10^{-2}$ mol.) and that the aconitic acid was able to give from 2 molecules 3 of fumaric acid, and hence a maximum of $2·04 \times 10^{-2}$ mol/litre of fumaric acid, it was calculated, assuming that the whole of the aconitic acid was transformed into the fumaric acid, that 35·8 per cent. of the fumaric acid formed was absorbed by the carbon.

Another confirmative experiment was done, shaking 0·0147 gm. of aconitic acid in 5 cc. of water with 0·11 gm. of activated carbon. As before 3 cc. of the filtered solution was neutralised with 0·22 cc. of lithium hydroxide 0·63 N. and diluted with 0·409 cc. of 0·884 N. lithium chloride, to give 0·1 N. in lithium chloride. Also here a curve was obtained, showing the only presence of fumaric acid and the complete absence of aconitic acid. The wave obtained was of an intensity of $537·5 \times 10^{-7}$ amps., and making the calculation as before, it was found out that 36·63 per cent. of the fumaric acid was absorbed by the carbon.

The carbon agitation, therefore, of the trimer [CH. COOH]₃ with activated carbon is sufficient to depolymerise it and then to reform the dimer fumaric acid :

$$2[CH. COOH]_3 \rightarrow 3[CH. COOH]_2$$
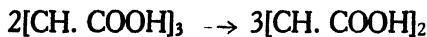
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A METHOD FOR THE ANALYSIS OF SOLUTIONS CONTAINING ZINC HYDROXIDE AND SODIUM HYDROXIDE

By

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LUNGE (Zeit. anorg. Chem., 1890, 227) developed a method for the analysis of solutions containing sodium hydroxide and aluminium hydroxide. In this method such a solution is titrated against standard hydrochloric acid using phenolphthalein and methyl orange as indicators. The end point obtained with phenolphthalein gives the alkali content of the solution while that obtained with methyl orange gives the amount of aluminium oxide.

Fricke (Zeit. Electro Chem., 1920, 26, 141) used the same method for the estimation of alkali in solutions containing alkali aluminate but added that the solution should be diluted and that best results are obtained from hot solutions. Müller (ibid., 1927, 33, 135) used this method for the analysis of alkali in solutions of sodium zincate.

Fricke and Humme (Zeit. anorg. Chem., 1928, 172, 234) gave the following procedure for the estimation of sodium hydroxide in a solution containing zinc hydroxide and sodium hydroxide.

A known volume of the solution diluted to about 100 to 150 times, was briskly shaken and titrated against a standard acid using phenolphthalein as indicator. After the colour disappeared, the solution was cautiously heated when the red colour reappeared. The solution was again titrated till the colour vanished once again. According to these authors, a careful titration of such a type requires, on an average, about 8 to 12 hours, and it gives results within 1 to 2·5 per cent. of those obtained gravimetrically by the estimation of sodium sulphate after the removal of zinc as zinc sulphide. The zinc content of the above solution was determined by precipitating it as zinc carbonate and weighing it as zinc oxide.

In view of the fact that there is no other method described in literature for strongly alkaline solutions containing zinc hydroxide and the accuracy attainable by this method has not been commented upon so far, it was considered interesting to work out and try other methods. As a result of these attempts, the method described below was evolved and it is found to give satisfactory results in a shorter time than required in the method of Fricke and Humme (loc. cit).

A measured volume of the solution containing zinc hydroxide and sodium hydroxide was treated with standard sulphuric acid (0·2 N to 0·3 N) and diluted to a known volume. In this solution zinc was estimated volumetrically by the method due to Cone and Cady (Journ. Amer. Chem. Soc., 1927, 49, 356) using potassium ferrocyanide as the standard titrating solution with diphenyl benzidine as an internal indicator.

Sodium sulphate present in the solution does not interfere [vide, Kolthoff and Pearson, Journ. Ind. Eng. Chem., (analytical volume) 1932, 147] and the method is very satisfactory as will be seen from the results given below.

An important point in this method is that the solution to be titrated should be heated to about 50° C to 60° C. Cone and Cady, (loc. cit.) state that the indicator decomposes in hot solutions, but Kolthoff and Pearson (loc. cit.) have shown that more accurate results are obtained in hot solutions.

For the estimation of sodium hydroxide " the sulphuric acid solution " was titrated with freshly standardised solution of ammonia using methyl red as indicator to estimate free sulphuric acid. The amount of sulphuric acid present in excess and that used up in reacting with zinc hydroxide being calculated, the quantity of the acid required to neutralise sodium hydroxide was easily obtained.

Experiments were also carried out using standard sodium hydroxide in place of ammonia with phenolphthalein as indicator. Since, however, zinc hydroxide precipitated before the end point was reached, ammonium chloride was added and titrations conducted in the usual manner. But it was found that the amount of sodium hydroxide required to neutralise the free sulphuric acid was far greater than the expected value.

EXPERIMENTAL

Three solutions containing different quantities of zinc oxide (Kahlbaum's pro analysi) and sodium hydroxide were prepared for analysis as follows :—

(1) A solution containing 50 ccs. of 8 N NaOH and 1·983 g. of zinc oxide.

(2) A solution containing 50 ccs. of 6 N NaOH and 1·5008 g. of zinc oxide.

(3) A solution containing 100 ccs. of 4 N NaOH and 0·9868 g. of zinc oxide.

Concentrations lower than 4N were not used because the method given in this paper is intended for strongly alkaline solutions and in dilute solutions the analysis can be carried out by the ordinary method without any difficulty.

In the above solutions, zinc was estimated gravimetrically as oxide and pyrophosphate as well as volumetrically according to the method of Cone and Cady (loc. cit.).

The sodium hydroxide content of the solutions was determined by the method described in this paper as well as by the method of Fricke and Humme (loc. cit.).

The results are given in tables 1 and 2 in which the mean values of duplicate estimations carried out in each case, have been given.

TABLE 1

Normality of NaOH solution	Zinc oxide dissolved in the solution	Zinc oxide found		
		Volumetrically with standard $K_4Fe(CN)_6$	Gravimetrically by Carbonate method	Gravimetrically by pyrophosphate method
8	1·983 g.	1·984 g.	1·961 g	1·970g.
6	1·5008g.	1 500 g.	1·4835g.	1 488g.
4	0·9868g.	0·9842g.	0·9750g.	0 991g.

TABLE 2

Normality of NaOH solution	Grams/litre NaOH	NaOH in grams/litre found	
		Fricke and Humme's method	Method described in this paper
8	320	310·72	321·2
6	240	234·56	240·9
4	160	157 96	159·1

The data in the above tables show that the method described in this paper gives better results than those obtained by the method due to Fricke and Humme (loc. cit.). It is also of interest to point out here that the methods of estimation of the alkali and zinc content of the solutions of zinc hydroxide in those of sodium hydroxide described above do not require more time than in ordinary titrations.

Although for the sake of brevity the data obtained with three typical concentrations have been given the method herein described was tested for higher concentrations and was found to give satisfactory results.

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STUDIES IN HYDROLYSIS

Comparison of the saponification constants of the cresyl esters of fatty Acids with those of the corresponding completely reduced Compounds, namely, the Methyl-Cyclohexyl esters of the same fatty Acids.

By

B. E. Mirza and G. D. Advani

THE saponification constants of the fatty and aromatic acids with Ethyl and Methyl alcohols by means of alkali hydroxides have been studied by many investigators. They have made particular reference only to the influence individually of the acid and the alcohol on the rate of saponification, the influence of solvents on the velocity constants, and the comparison of the velocity constants of certain esters in different solvents.

Findlay and Turner (Jour. Chem. Soc. 87, 747, 1905) and Findlay and Hickmans (*Ibid.* 95, 1004, 1909) have compared the velocity of saponification of certain esters in water and alcohol containing varying amounts of water. Anderson and Brown (Jour. Phys. Chem. 20, 195, 1916) compared the velocity of saponification of fats and oils in different solvents. Anderson and Pierce (*Ibid.* 22, 44, 1918) have compared the velocity constants of certain esters in three different alcohols. But a detailed study of the subject has shown that no attempt has ever been made to find the velocity of saponification of the Cresyl and Phenyl esters and their completely reduced derivatives.

The object of the present investigation has been to determine the saponification constants of Cresyl and Methyl-cyclohexyl esters of the fatty acids and to know whether there is any relationship generally existing (1) between the saponification constants of the above mentioned saturated and completely reduced esters and (2) between the esters of one alcohol with homologous acids.

EXPERIMENTAL

The preparation of Reagents

(1) *Solvent.*—The solvent used was 93 per cent. neutral Ethyl alcohol by weight. Before using it was purified by silver nitrate and potassium hydroxide to get rid of any impurities like free acids and aldehydes.

(2) *Alcoholic Potash.*—Alcoholic Potassium hydroxide was prepared by dissolving the necessary quantity of pure Potassium hydroxide sticks (E. Merck) in a small quantity of distilled water and adding the same to the required quantity of pure alcohol to make 1/5th normal solution

It was allowed to stand so that small amounts of the precipitate of Potassium carbonate may settle down and was then rapidly filtered. The solution was then standardised with 0.1026 normal hydrochloric acid. Enough quantity of the solution was made to suffice for all the experiments in this investigation.

(3) *Esters.*—All the Methyl-cyclohexyl esters were supplied by " Poulene Freres, France." They were purified by redistillation before use.

All the Cresyl esters except Ortho-cresyl Butyrate and Meta-cresyl Butyrate were prepared in the laboratory according to the directions given in Beilsteins dictionary and were purified until they had the correct boiling points. The two esters mentioned above are not described in literature and so were prepared by us. (A description of their preparation and some of the properties studied by us will be dealt with in a separate paper).

SAPONIFICATION PROCEDURE

The procedure adopted in saponifying the Esters is described below :

In a measuring flask of 100 c.c. capacity was placed the volume of ester, which was slightly less than that which could be saponified by 200 c.c. of 0.1 normal Potassium hydroxide. With the ester in the flask the volume was made up to 100 c.c. by adding pure distilled alcohol, which had already been brought to the temperature of the thermostat. The latter was so adjusted as to keep the temperature constant at $35°$ C and in which the temperature was maintained constant within $0.01°$ C for days together. The ester solution was then transferred to 250 c.c. pyrex glass bottle and again placed in the thermostat. A second 100 c.c. measuring flask containing 0.2002 normal alcoholic Potassium hydroxide was also placed in the same thermostat side by side for sufficiently long time for the solution to attain the constant temperature. After this they were mixed into the pyrex glass bottle and was again kept in the thermostat. The time of mixing was carefully noted. By following this procedure the ester was in every case being saponified by 0.1001 normal alcoholic KOH. At suitable intervals, which depended on the velocity of particular reaction, 10 c.c. of it were withdrawn and run into 10 c.c. of 0.1026 normal HCl, the time being noted. The excess of HCl was then titrated with 0.1002 normal KOH solution (aqueous). The 0.1002 KOH was kept in the burette of 10 c.c. capacity graduated directly to 0.02 c.c., but which could be easily read to 0.005 c.c.

CALCULATIONS

The Velocity constants were calculated by making use of the equation for reactions of the second order.

RESULTS AND DISCUSSION

In Table I below are given the saponification constants of all the esters saponified by 0·1001 normal Potassium hydroxide.

TABLE I

Names of Esters	Saponification constants in 2 exp.	Mean Sap. Constants
Ortho-cresyl Acetate	0·0002743 0·0002716	0·0002729
Meta-cresyl Acetate	0·0003137 0·0003014	0·0003075
Para-cresyl Acetate	0·0003571 0·0003570	0·0003571
Ortho-cresyl Propionate	0·0001251 0·0001277	0·0001264
Meta-cresyl Propionate	0·0001144 0·0001138	0·0001141
Para-cresyl Propionate	0·0001239 0·0001250	0·0001245
Ortho-cresyl Butyrate	0·00008641 0·00009433	0·00009037
Meta-cresyl Butyrate	0·00006843 0·00006792	0·00006817
Para-cresyl Butyrate	0·00007751 0·00007722	0·00007737
Ortho-methyl Cyclohexyl Acetate	0·0008930 0·0008929	0·0008929
Meta-methyl Cyclohexyl Acetate	0·003174 0·003154	0·003164
Para-methyl Cyclohexyl Acetate	0·003540 0·003549	0·003545
Ortho-methyl Cyclohexyl Propionate	0·0003139 0·0003093	0·0003116
Meta-methyl Cyclohexyl Propionate	0·001144 0·001116	0·001130
Para-methyl Cyclohexyl Propionate .. .	0·001256 0·001243	0·001249
Ortho-methyl Cyclohexyl Butyrate	0·0001917 0·0001794	0·0001855
Para-methyl Cyclohexyl Butyrate	0·0007844 0·0007749	0·0007797

It is apparent from the above Table that the velocity of Saponification of the cresyl esters is always less than that of the corresponding methyl-

cyclohexyl esters. This shows that the completely reduced compounds are far more active than the unreduced compounds. This is as it should be, because the completely reduced esters belong to the poly-methylene series and resemble the aliphatic compounds in their properties. They are hydrolysed more quickly than the corresponding esters containing the same number of carbon atoms in the aromatic series.'

It is generally found that the velocity constants of the ortho esters are always less than those of the corresponding meta and para compounds, possibly due to steric hindrance. The results in Table I indicate that it is also true in the case of the methyl cyclohexyl esters in as much as the velocity constants of the meta and para isomers are about four times as great as those of the corresponding ortho ester. But in the case of cresyl esters it is found that the ortho esters are saponified much more quickly than the corresponding meta and para compounds. Here the velocity constant of the ortho-cresyl acetate is only a little less than those of the meta and para compounds, while the velocity constants of ortho-cresyl propionate and ortho-cresyl butyrate are actually higher than those of the corresponding meta and para compounds. It is difficult to assign any explanation for this anomaly at the present time but it may probably be due to the acidic nature of the cresyl group.

In Table II below are given the saponification constants of the methyl-cyclohexyl esters and their corresponding cresyl esters of the different acids. In the third column are given the ratios of the former to the latter.

TABLE II

Names of Esters				Saponification Constants	Ratio
Para-methyl cyclohexyl acetate	..	..	..	0·003545	9·926
Para-cresyl acetate	..	..	..	0·0003571	
Meta-methyl cyclohexyl acetate	..	..	..	0·003164	10·29
Meta-cresyl acetate	..	..	..	0·0003075	
Ortho-methyl cyclohexyl acetate	..	..	..	0·0008929	3·272
Ortho-cresyl acetate	..	..	..	0·0002729	
Para-methyl cyclohexyl propionate	..	.	..	0·001249	10·03
Para-cresyl propionate	..	..	..	0·0001245	
Meta-methyl cyclohexyl propionate	..	..	..	0·001130	9·904
Meta-cresyl propionate	..	..	..	0·0001141	
Ortho-methyl cyclohexyl propionate	..	..	.	0·0003116	2·465
Ortho-cresyl propionate	..	..	..	0·0001264	
Para-methyl cyclohexyl butyrate	..	..	..	0·0007797	10·08
Para-cresyl butyrate	..	..	..	0·00007737	
Ortho-methyl cyclohexyl butyrate	..	..	..	0·0001855	2·052
Ortho-cresyl butyrate	..	..	.	0·00009037	

It can be seen from the third column of the Table II that the ratio between the para and meta isomers is nearly the same, that is 10, but the ratio of the corresponding ortho esters is very low and ranges between 3·27 and 2·052.

In Table III are given the ratios of the esters of one alcohol with homologous acids.

<div align="center">TABLE III</div>

Names of Esters				Saponification Constants	Ratio
Para-methyl cyclohexyl acetate	..	..	..	0·003545	2·839
Para-methyl cyclohexyl propionate	..	..	..	0·001249	
Meta-methyl cyclohexyl acetate	..	..	..	0·003161	2·797
Meta-methyl cyclohexyl propionate	..	.	..	0·001130	
Ortho-methyl cyclohexyl acetate	..	..	..	0·0008929	2·865
Ortho-methyl cyclohexyl propionate	..	..	..	0·0003116	
Para-methyl cyclohexyl propionate	..	..	..	0·001249	1·602
Para-methyl cyclohexyl butyrate	..	..	..	0·0007797	
Ortho-methyl cyclohexyl propionate	..	..	..	0·0003116	1·680
Ortho-methyl cyclohexyl butyrate	..	..	..	0·0001855	
Para-cresyl acetate	..	..	..	..	0·0003571	2·868
Para-cresyl propionate	..	..	..	..	0·0001245	
Meta-cresyl acetate	..	..	..	..	0·0003075	2·694
Meta-cresyl propionate	..	..	..	.	0·0001141	
Ortho-cresyl acetate	..	..	..	..	0·0002729	2·158
Ortho-cresyl propionate	..	..	..	.	0·0001264	
Para-cresyl propionate	.	..	..	..	0·0001245	1·609
Para-cresyl butyrate	..	..	..	..	0·00007737	
Meta-cresyl propionate	..	..	..	..	0·0001141	1·674
Meta-cresyl butyrate	..	..	..	..	0·00006817	
Ortho-cresyl propionate	..	..	..	..	0·0001264	1·399
Ortho-cresyl butyrate	..	..	..	..	0·00009037	

It is a well known fact that the saponification constants of the esters of one alcohol with acetic acid are respectively greater than those of the corresponding esters with propionic acid and those of propionic acid are greater than those of butyric acid.   Here also we find the same regularity. We can further say that the acetic acid esters are saponified about 2·8 times faster than those of the corresponding esters of propionic acid and those of propionic acid are about 1·6 times faster than those of butyric acid.   The ratios of the saponification constants of ortho-cresyl acetate to ortho-cresyl propionate and of ortho-cresyl propionate to ortho-cresyl butyrate are much lower than those of others.

As there is a constant ratio between the completely reduced and un-reduced esters of the homologous acids and also between the esters of one alcohol with homologous acids, the problem of the determination of velocity of saponification is rendered very simple. They can be very easily found by mathematical calculations after finding by experiment only one of them. But separate determinations are to be made for ortho esters.

To prove our point still further we have found the above relationship for the Phenyl and its completely reduced derivatives, namely, cyclohexyl esters, which will be dealt with in a separate paper.

The authors take the opportunity of thanking Dr. J. V. Lakhani for valuable suggestions in the course of the above work.

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES

Part XIV—The Condensation of 2 : 4-Dinitro-benzaldehyde : The Influence of Nitro Groups

By

K. C. PANDYA, P. I. ITTYERAH AND MISS R. K. PANDYA

IN Part XIII of the series (Pandya and Miss Pandya, *Pro. Ind. Acad. Sci.*, A, 1941, *13*, 112) it was shown that while the presence of one chlorine or one bromine atom on the ring results in an increase of the yield in the condensations carried out by Perkin's method and the pyridine-trace method, the yields by the pyridine-trace method were considerably better and that this method had also other points of advantage over Perkin's method.

In the present paper the influence of one nitro-group as well as of two nitro-groups on these condensations has been studied.

The data for the condensations of the three nitro-benzaldehydes by Perkin's method is obtainable in the paper of Lock and Bayer (Lock and Bayer, *Ber.*, 1939, *72*, 1064) who give the following figures as the yields of o-, m- and p-nitro-cinnamic acids obtained by Perkin's method :

$$75 \qquad 75 \qquad 82 \text{ per cent.}$$

The yields obtained by the pyridine method have also been reported by different workers and are very much larger besides being obtained in a much simpler way. Thus,

	Ortho	Meta	Para
Surange (Pandya and Surange *J. I. C. S.*, 1934, 11, 824) got	96	93	90 per cent.
Kurien (Kurien and Pandya, *ibid*, 825) got ..	....	92	....
Dilbahar Singh (Dilbahar Singh and Pandya, *Pro Ind. Acad. Sci*, A, 1939, 9, 566) got ..	91	88	88 per cent.

Surange had obtained his high yields by heating with a full molecular proportion of pyridine for only two hours, while Kurien and Dilbahar Singh had used the pyridine-trace with only four hours' heating on the waterbath, in contrast with the minimum eight hours' heating at 180° required for Perkin's reaction.

As unsubstituted benzaldehyde gave only a 49 per cent. yield of cinnamic cid by Perkin's method under standardised conditions (Meyer

and Beer, *Monatsch*, 1913, 34, 210), Lock and Bayer are justified in concluding that the influence of the nitro-group is to increase the yield of the condensation-product in Perkin's reaction. Strictly speaking, the same conclusion cannot be drawn in the case of the pyridine-trace method. Because here the yield of cinnamic acid from unsubstituted benzaldehyde is itself 95 per cent. (Pandya and Pandya, loc. cit.), i.e., only a little less than the theoretical, and the yields from the nitro-benzaldehydes are slightly, though only slightly, less. Yet there is a clear indication that the reaction itself is quickened, particularly if a full molecular quantity of pyridine is employed. A mere trace of pyridine is enough to catalyse the condensation, but the remaining amount of the base, probably, acting as a stable solvent, prevents decomposition which invariably sets in if the reaction is allowed to become too energetic.

Regarding the polynitro-benzaldehydes, Lock and Bayer state (loc. cit.) that in the Perkin's reaction they react so energetically that complete decomposition occurs under the standardized conditions and that, under milder conditions, dinitrocinnamic acid is formed, but that, even under those conditions, the preparation of 2 : 4 : 6-tri-nitrocinnamic acid is not successful. The yields of the dinitrocinnamic acid are not given and may be presumed to be small.

The condensation of one of the three known dinitrobenzaldehydes, namely, the 2 : 4-dinitrobenzaldehyde, with malonic acid has now been fairly exhaustively studied in this laboratory and the results are presented in this paper. 2 : 4-Dinitrobenzaldehyde has been condensed to give the 2 : 4-dinitrocinnamic acid by Perkin's reaction by Friedländer and Fritsch (Friedländer and Fritsch, *ibid*, 1902, 23, 534) who also report having prepared 3 : 4-dinitrobenzylidenemalonic acid bv the condensation of the aldehyde with malonic acid in the presence of acetic acid, as early as in 1902.

When one obtains o- and p-nitrocinnamic acids from the o- and p-nitrobenzaldehydes in about 90 per cent. yields, one naturally expects that the o-p-dinitrobenzaldehyde would react more quickly and give at least 90 per cent., probably a higher, yield of the dinitrocinnamic acid. This expectation was not realized. Under milder conditions no reaction could be detected as having occurred, the aldehyde being recovered unchanged almost wholly, sometimes with malonic and sometimes with acetic acid. Traces of pyridine, of piperidine and of lutidine were tried separately mostly without success. Higher temperatures and longer heatings, as well as the use of Robinson's pyridine-piperidine mixture led inevitably to decomposition, charring and resinification. The usual method of heating on a waterbath for' four hours with a trace of pyridine entirely failed, the aldehyde showing a remarkable stability and a total lack of reactivity. Ultimately appreciable yields were obtained by suitable adjustments of conditions ; the highest yield (50 per cent.) resulted from heating for four hours at first on the waterbath and for another four hours in an oilbath between 105° and 110°.

The 2 : 4-dinitrobenzylidenemalonic acid, reported by Friedländer (loc. cit.) as crystallising with one molecule of water, the hydrate melting at 49°,

was not obtained when the aldehyde and malonic acid were heated together, either alone or in the presence of acetic acid.

There is thus no doubt about the peculiarly diminished reactivity of the aldehyde group when two nitro-groups are present on the ring in ortho and para positions to the aldehyde. The cause of this is not clear. It would also be interesting to see whether the other isomers, the 3 : 5 and the 2 : 6 dinitrobenzaldehydes would behave similarly.

Another independent confirmation of this peculiarity is available from the aldehyde-amide condensations investigated in this Laboratory, where the dinitrobenzaldehyde and the mono-nitro-benzaldehydes exhibit similar behaviour in their condensations with different amides (Ittyerah and Pandya, under publication).

<div align="center">

EXPERIMENTAL

(With P. I. Ittyerah)
</div>

The 2 : 4-dinitrobenzaldehyde was prepared according to the method of Bennett and Bell (Bennett and Bell, *Organic Synthesis, XII,* 1932, 30). The yield of the crude aldehyde was good, but during recrystallisation a considerable loss occurred. [Could this be due to the action of light, which, according to Cohn and Friedländer (Cohn and Friedländer, *Ber.* 1902, *35,* 1265) changes it into o-nitroso-p-nitrobenzoic acid ?]

Condensation in the absence of any Condensing Agent.—Four experiments were made under different conditions :—

(*i*) 0·5 g. malonic acid and 1·0 g. aldehyde were mixed and heated on the waterbath for four hours. On cooling, the mass, which was a yellow liquid, was extracted with sodium carbonate solution, and then the alkali extract was acidified. No acid was obtained, while most of the aldehyde was recovered.

(*ii*) The same materials were heated at 105–110° for four hours. About half of the aldehyde used was recovered, unchanged except a little in colour, no other product being isolated.

(*iii*) The aldehyde and the acid, in molecular proportions as above, were heated together on the waterbath for twelve hours. The dinitro-benzaldehyde was recovered almost quantitatively, with a little of malonic acid.

(*iv*) The above experiment was repeated at 110°, with eight hour ' heating : the result was exactly the same.

Condensation in the presence of Acetic Acid.—1·0 g. dinitrobenzaldehyde, 0·5 g. malonic acid and 0·5 c.c. glacial acetic acid were mixed and heated on the waterbath for six hours. On the usual treatment being given, 0·9 g. of the aldehyde and a little of malonic acid were recovered, without any other acid such as the dinitrobenzylidenemalonic (Friedländer and Fritsch, loc. cit.).

Condensation in the presence of Pyridine.—(*i*) 1·0 g. aldehyde, 0·5 g. acid and a drop of pyridine were mixed, shaken and kept in a flask at room temperature for two months. The contents were examined when the dinitrobenzaldehyde was recovered almost quantitatively.

(*ii*) 2·0 g. dinitrobenzaldehyde, 1·0 g. malonic acid and a trace of pyridine were heated together on the waterbath for four hours. The usual treatment yielded only a negligible amount of any product.

(*iii*) The same experiment was repeated, but the heating was prolonged for eight hours. At the end, the reacting material, when cold, did not solidify as before to a yellow mass, but remained a dark red liquid. On the addition of water, however, for extraction, the whole mass solidified : further extraction gave 0·3 g. of the dinitrocinnamic acid, i.e., 25 per cent. yield. On recrystallisation, it melted at 179° which agrees with the melting point of Friedlander (loc. cit.).

(*iv*) The same experiment repeated so that the heating was at 105–110° for four hours, increased the yield to 29 per cent.

(*v*) The heating was then continued for six hours at 105–110°. The yield of the dinitrocinnamic acid was only 0·1 g., or 9 per cent. of theory.

(*vi*) On heating for eight hours at 105–110°, much charring took place and the brownish red liquid left gave only a trace of the acid.

(*vii*) The three were taken in the same amounts and heated in an oil-bath in such a way that the temperature rose from 100° to 150° in the course of 1·5 hours, the heating being continued at the higher temperature for another five hours. 0·6 g. aldehyde was recovered, no other product could be isolated.

(*viii*) 2·0 g. aldehyde, 1·1 g. malonic acid and two drops of pyridine were well mixed and heated on a waterbath for four hours : there was a slight effervescence at the start, but it had stopped at the end. The heating was continued thereafter at 105–110° for another four hours after which the yield obtained was the largest ever obtained, viz. 1·2 g. or 50 per cent. of theory.

(*ix*) The reaction-mixture was kept in separate flasks, as in (*i*) above, with a trace of piperidine, lutidine, and ethanolamine respectively in place of pyridine, for three weeks. At the end, the mass had resinified a little, but gave nothing of the acid.

(*x*) Treated with a trace of piperidine and of lutidine respectively, on the waterbath for four hours, the mass became black and tarry, from which nothing could be separated.

Condensation with Pyridine-Piperidine Mixture.—0·5 g. aldehyde, 0·75 g. acid, 0·6 c.c. pyridine and a drop of piperidine were mixed and heated on the waterbath for two hours. There was much effervescence. The heating was concluded with a gentle heating on a free flame for about thirty minutes. Test-portions were taken out at intervals. None of these, not even the tarry liquid left at the end and smelling strongly of acetic acid,

gave any of the expected product, though a little of the aldehyde was recovered. The conditions under which the maximum yield was obtained were tried again, (*viii*) above, but without pyridine or any other base or condensing agent : no condensation seemed to have taken place.

(*With Miss Rashmi Bala K. Pandya*)

The following, among several methods tried, gave the best yield :— 1·96 g. dinitrobenzaldehyde, 1·04 g. malonic acid and 0·14 c.c. pyridine were heated on waterbath. Effervescence started immediately and continued nearly for four hours. After six hours' heating, the flame was removed and the flask was left overnight. The dark red plastic mass was washed with ether to remove the unchanged aldehyde, and the remaining acid was dissolved in hot sodium carbonate solution and filtered. Some of the aldehyde was also separated by this means. The filterate on being acidified with hydrochloric acid gave a brown precipitate, which on drying melted at 165°, and on recrystallisation from benzene, melted at 179°. Yield 42 per cent.

SUMMARY

2 : 4-Dinitrobenzaldehyde is condensed with malonic acid with success only under special conditions wnich require the presence of a trace of pyridine. The yield is then 50 per cent. of the theoretical. The two nitro-groups in the ortho and para positions respectively to the aldehyde group appear to restrain considerably the usual reactivity of the aldehyde group with malonic acid.

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SOME NEW REACTIONS OF 1-BENZYLIDENE-COUMARAN-2-ONES, Part II

By

T. B. PANSE, R. C. SHAH AND T. S. WHEELER

IT was observed that the reactions characteristic of the keto-ethylene group, exhibited by chalkones are unaffected by the partially cyclised keto-ethylene group in l-p-anisyli denecoumaran-2-one (Panse, Shah and Wheeler, Part I, J.I.C.S., in press). In order to confirm this observation further, a study of the reactions of chalkones with another benzylidenecoumaran-2-one was deemed necessary. Work was, therefore, continued on 5-methoxy-1-anisylidenecoumaran-2-one (I) and it is found that all the typical reactions of chalkones could also be realised on it, as on the previous one.

Thus (I), on bromination forms a dibromide (II), the bromine atom in which, like the halogen atom in phenyl-p- or o-alkoxystyryl ketone dibromides (alkoxychalkons dibromides), is readily replaced by alkoxyl on treatment with alcohols (see Warrair, $et. al.$, J.C.S., 1937, 1798) and the resulting product has been assigned the constitution (III), viz., a-bromo-3-alkoxy-derivative of (II).

(I) like chalkones also undergoes normal Michael addition with cyclohexanone and desoxybenzoin (see Hill, J.C.S., 1935, 1115) to yield (IV) and (V) respectively.

(I) like chalkones also condenses with ethyl -aceto-acetate to give a cyclohexanone derivative (VI) (see Knoevenagel, Ann., 1894, 281, 58). The structure assigned to (VI) is based on the chalkone analogy (see Rao and Wheeler, J.C.S., 1939, 1004) and is supported by its reactions with dinitrophenyl hydrazine and similar other ketonic reagents.
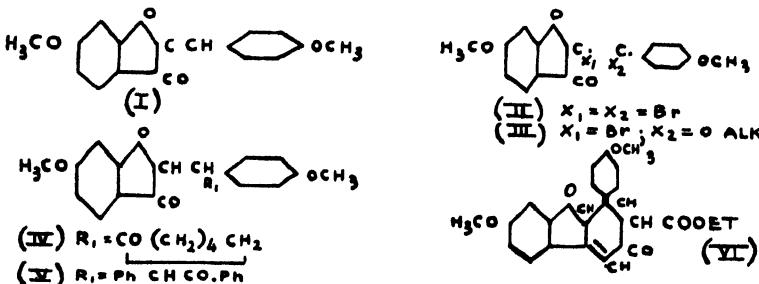
EXPERIMENTAL

2-Acetoxy-4-methoxyphenyl-p-methoxystyryl ketone was prepared as described by Kostanecki and Osius (Ber., 1899, 32, 322).

$Bromination$ of 2-$acetoxy$-4-$methoxyphenyl$-p-$methoxystyryl$-$ketone$.— 2-Acetoxy-4-methoxyphenyl-p-methoxystyryl ketone was dissolved in

carbontetrachloride solution in cold and the theoretical quantity of
15 per cent. bromine solution, in the same solvent was added to it.
Removal of the solvent left 2-acetoxy-4-methoxyphenyl-a β-dibromo-
β-p-anisylethyl ketone. On crystallization from light petroleum, it
melted at 143°C. (Found : Br, 32·9 ; $C_{19} H_{18} O_5 Br_2$ requires Br.
32·9 per cent.).

Preparation of 5-methoxy-1-p-anisylidenecourmaran-2-one.—The 2-
acetoxy-4-methoxyphenyl-a =β-dibromo-β-p-anisylethyl-ketone (50   g.)
was boiled with alcohol (250 c. c.) for one hour, so that the corresponding
bromo-ethoxy compound was formed in solution (see Warriar, *et. al.*,
J. C. S., 1937, 1798). To this solution while hot was added 10 per cent.
solution of potassium hydroxide (250 c. c.). On cooling the reaction,
liquid 5-methoxy-1-p-anisylidenecoumaran-2-one separated. It was
filtered, washed with water and crystallized from alcohol in yellow needles
melting at 134°C. (Found : C, 72·4, H, 5·0 , $C_{17} H_{14} O_4$ requires
C, 72·3, H, 5·0 per cent.).

Bromination of 5-methoxy-1-p-anisylidenecoumaran-2-one.—(I) when
treated with cold chloroform solution with the theoretical quantity of
bromine in the same solvent yielded 1-bromo-5-methoxy-1-(w-bromo-p-
methoxybenzyl)-coumaran-2-one (II), m.p. (carbon tetrachloride) 161°C.
Found : Br, 36·4 ; $C_{17} H_{14} O_4 Br_2$ requires Br, 36·2 per cent.).

Action of alcohols on 5-methoxy-1-p-anisylidene-coumaran-2-one.—The
dibromide (II) when boiled with methyl or ethyl alcohol for half an hour
gave respectively on cooling, 1-bromo-5-methoxy-1-(w, p-dimethoxy-
benzyl)-coumaran-2-one, m.p. (methyl alcohol) 131°C (Found : Br, 21·0 ;
$C_{18} H_{17} O_5$ Br. requires Br, 20·4 per cent.) ; and 1-bromo-5-methoxy-1-
(p-methoxy-w-ethoxybenzyl)-coumaran-2-one, m.p. (alcohol) 139°C.
(Found : Br, 20·3 ; $C_{19} H_{19} O_5$ Br. requires Br, 19·7 per cent.).

*Condensation of 5-methoxy-1-p-anisylidene-coumaran-2-one with
cyclohexanone.*—To a boiling alcoholic solution of (I) (5 g.) and
cyclohexanone (10 c.c.) was added an aqueous sodium hydroxide solution
(50 per cent., 10 g.) On allowing to cool the reaction liquid overnight
5-methoxy-1-[p-methoxy-W-(2'-keto-1'-cyclohexyl) benzyl] coumaran-2-
one, separated. It was filtered, washed with water and crystallized from
alcohol when it melted at 182°C (decomp.). (Found : C, 71·5 ; H, 6·1 ;
$C_{23} H_{24} O_5$, ½ H_2 O requires C, 71·0, H, 6·4 per cent.).

*Condensation of 5-methoxy-1-p-anisylidenecoumaran-2-one with desoxy-
benzoin.*—The alcoholic solution of (I) (5 g.) and of desoxybenzoin (5 g.)
were mixed and heated at the boiling point for half an hour. While still
hot, sodium ethoxide (1·25 gm. sodium) was added to it. The reaction
mixture on cooling yielded 5-methoxy-1-(-benzoyl-s-phenyl-a-p-
anisyl-a-ethyl)-coumaran-2-one (V) in crystalline form. It was
recrystallized from a mixture of acetone and chloroform and melted at
273°C. (Found : C, 74·9, H, 5·7 ; $C_{31} H_{26} O_5$, H_2 O requires C, 74·8,
H, 5·6 per cent.).

Condensation of 5-methoxy-1-p-anisylidene-coumaran-2-one with ethyl acetoacetate.—An alcoholic of solution (I) (5 g.) ethyl acetoacetate (6·3 c.c.) and sodium ethoxide (0·62 g. sodium) were heated under reflux for four hours and kept overnight. Next day crystals of etyl-2-p-anisyl-3 : 4 [1' : 2'–(5' methoxy-coumarano)]-Δ4-cyclohexen-6-one-1-carboxylate (VI), separated from the solution. On crystallization from alcohol, it melted at 146°C. (Found : C, 70·2 ; H, 5·6 ; $C_{23} H_{22} O_6$ requires C, 70·1 ; H, 5·6 per cent.). It gave cherry red colouration with alcoholic ferric chloride.

Hydrolysis and decarboxylation of ethyl-2-p-anisyl-3 : 4 1': 2'–(5'-methoxycoumarano)]-Δ4-cyclohexen-6-one-1-carboxylate.—The condensation of product (VI) (0·5g.) was heated with 10 per cent. hydrochloric acid (20 c. c.) in sealed tube, under pressure at 160°C for five hours. On cooling the contents of the tube was obtained a sticky mass which was separated by filtration, washed with water and sodium bicarbonate. The 5-p-anisyl-3 : 4-[2': 1'-(5'-methoxycoumarano)]-Δ2-cyclohexen-1-one, so obtained was crystallized from alcohol in needles m.p. 154°C. (Found : C, 74·2 ; H, 6·1 ; $C_{20} H_{18} O_4$ requires C, 74·4, H, 5·6 per cent.).

(VI) also yielded the following derivatives :—

Semicarbazone, m.p. (after being washed with hot alcohol) 246°C (decomp.). (Found : N, 9·2 per cent ; $C_{24} H_{25} O_6 N_3$ requires N, 9·3 per cent.) ; *Oxime*, m. p. (80 per cent. alcohol) 142°C. (Found : N, 3·4 ; $C_{23} H_{23} O_6 N$ requires N, 3·5 per cent.) ; *2 : 4-dinitrophenylhydrazone* (yellow crystals) m.p. (acetic acid) 192°C. (Found : N, 9·7 ; $C_{29} H_{26} O_9 N_4$ requiies N, 9·8 per cent.) ; the *copper salt* of (VI) which was obtained by shaking (VI) in ethereal solution with an equal weight of copper acetate in aqueous solution for six hours, had, after being washed with hot water, a melting point 215°C. It is soluble in benzene. (Found : Cu, 7·3 ; $(C_{25} H_{21} O_6) 2$ Cu requires Cu, 7·4 per cent.).

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THE CONDENSATION OF α-SUBSTITUTED ACETO-ACETATES WITH PHENOLS, PART V-COUMARINS FROM SOME ALKYL-RESORCINOLS AND ETHYL-PYROGALLOL AND ETHYL α-(α-HYDROXY-βββ-TRICHLORO-ETHYL)-ACETOACETATE

By
N. M. Shah and D. R. Kulkarni

IN continuation of our work on the effect of α-substituents (other than alkyl) in the acetoacetate molecule on the course of the Pechmann condensation (Shah N. M. and Shah R. C., Ber. 1938, 71, 2075 ; Shah N. M., J. Univ. Bom., 1939, 8 (iii), 205 ; Kulkarni, Alimchandani and Shah N. M., J. Indian C. S., 1941, 18, 113, 123), the present investigation was undertaken with a view to study the influence of various constitutional factors in a phenol molecule in the above condensation. In this paper, we describe the condensation of ethyl α-(α-hydroxy-βββ-trichloro-ethyl)-acetoacetate with some 4-alkyl-resorcinols and 4-ethyl-pyrogallol. Before the present work could be extended to various substituted resorcinol and other phenol derivatives, it was not possible to continue the present collaboration ; the results so far obtained are therefore recorded.

Two 4-alkyl-resorcinols, viz., 4-ethyl-and 4-propyl-resorcinols were tried : Both of them condense with α-(α-hydroxy-βββ-trichloro-ethyl)-acetoacetate giving the corresponding 6-alkyl-7-hydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarins under the conditions of the Pechmann reaction. Sulphuric acid as a condensing agent gave very poor yields of the product ; and phosphorus oxychloride was found to be an efficient condensing agent. Aluminium chloride (Sethna, Shah and Shah, J. 1938, 228) was found to be unsuitable as tarry matter was produced, possibly due to side-reactions with the -CH(OH)CCl₃ group.
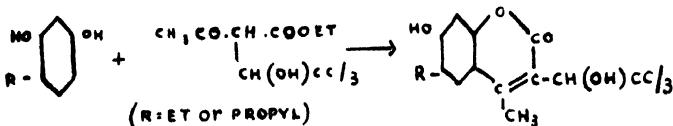
The behaviour of 4-ethyl-pyrogallol was similar to that of 4-ethyl-resorcinol ; it smoothly underwent the condensation with the above ester giving 6-ethyl-7 : 8-dihydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarin in presence of phosphorus oxychloride.

The above results show that 4-ethyl-resorcinol and 4-ethyl-pyrogallol are as reactive as resorcinol and pyrogallol in the above condensation, the alkyl group having no retarding influence on the course of the reaction. These results are in conformity with those of other workers (Desai and Ekhlas, Proc. Ind. Acad. Sc., 1938, 8, 567 ; Deliwala and Shah, ibid, 13, 352).

EXPERIMENTAL

7-Hydroxy-6-ethyl-3-(∝ -hydroxy-βββ-trichloro-ethyl) 4-methylcoumarin-
4-Ethyl-resorcinol was prepared according to Shah R. C. and Mehta
(J. Univ. Bom., 1935, **4** (*ii*), 109). The resorcinol (5 g.) and ethyl
∝ -(∝ -hydroxy-βββ-trichloro-ethyl)-acetoacetate (10 g.) were mixed and
phosphorus oxychloride (5 c. c.) added in small quantity at a time with
shaking. The mixture was kept cooled under tap, and then left overnight.
It was poured into ice-cold water and the substance that separated was
well washed with water, collected and crystallised from alcohol,
needles, m.p. 211–212° (decomp.); yield 3·5 g. (Found: Cl, 29·9.
$C_{14}H_{13}O_4Cl_3$ requires Cl, 30 3 per cent.). The *coumarin* dissolves in
alkaline solution exhibiting blue fluorescence characteristic of a
7-hydroxy-coumarin derivative. It also dissolves in conc. H_2SO_4 with
violet fluorescence.

It is soluble in common organic solvents but insoluble in petroleum
ether.

The above condensation was tried with sulphuric acid (80 per cent.)
as condensing agent by keeping it for 3 hours. The product obtained
on working it up was identical with the above coumarin. The yield was
very poor. If the period of the reaction is prolonged, a highly coloured
mass is obtained from which no crystalline product could be isolated.

The *acetyl* derivative prepared by acetic anhydride and a few drops
of conc. H_2SO_4, crystallised from alcohol in needles, m.p. 167°. (Found:
Cl, 24·3. $C_{18}H_{17}O_6Cl_3$ requires Cl, 24·5 per cent.).

The *benzoyl* derivative prepared by benzoyl chloride-pyridine method
crystallised from hot glacial acetic acid, small granules, m.p. 185–186°.
(Found: Cl, 18·63. $C_{28}H_{21}O_6Cl_3$ requires Cl, 19·0 per cent.).

The *methoxy* derivative prepared by dimethyl sulphate method in ice
separated a. yellowish solid on keeping overnight; crystallised from
alcohol, m.p. 167°. (Found: Cl, 27·7. $C_{16}H_{17}O_4Cl_3$ requires
Cl, 28·1 per cent.). The alkaline filtrate after removal of the above
methoxy derivative gave on acidification a substance (mono-methoxy
derivative) which was crystallised from rectified spirit, m.p. 231°
(decomp.). (Found: Cl, 28·87. $C_{15}H_{15}O_4Cl_3$ requires Cl. 29·14 per
cent.). It is easily soluble in alkali with violet fluorescence.

7-hydroxy-6-propyl-3-(∝ -hydroxy-βββ-trichloro-ethyl)-4-methyl-coumarin
—4-propyl-resorcinol was prepared by the Clemmensen reduction of
respropiophenone (Chakravarti and Chakravarty, J. Indian C. S., 1939,
16, 148). The resorcinol (2·5 g.) and the ester (5 g.) were condensed
as in the previous case in presence of $POCl_3$ (3 c.c.). A pasty mass
separated, which was repeatedly washed with cold water. It was dis-
solved in alcohol and left overnight when a small quantity of the white
solid was obtained ; first crystallised from alcohol and then from a mixture
of acetone and petrol benzine, clusters of thick needles, m.p. 189°.
The yield is low. (Found: Cl, 28·83. $C_{15}H_{15}O_4Cl_3$ requires Cl,

$29\cdot14$ per cent.). The *coumarin* dissolves in alkali as well as conc. H_2SO_4 with blue fluorescence.

The *acetyl* derivative prepared as usual crystallised from methyl alcohol, lustrous thin plates m.p. $132-134°$. (Found : Cl, $23\cdot53$. $C_{19}H_{19}O_6Cl_3$ requires $23\cdot7$ per cent.).

7 : *8-dihydroxy-6-ethyl-3-(∝ -hydroxy-ββ,β-trichloro-ethyl)-4-m e t h y l-coumarin*—4-ethyl-pyrogallol was prepared by the Clemmensen reduction of gallacetophenone (Clemmensen, Ber., 1914, *47*, 51 ; J. C. S., 1920, *117*, 973). The pyrogallol (2 g.) and the ester (4 g.) were mixed and to the mixture, $POCl_3$ (3-4 c.c.) was slowly added as before, and the mixture left overnight. On working it up by adding water, a solid separated which was washed first with water and then kept in contact with little alcohol which removed coloured impurities. The white residue was recrystallised from alcohol, fine powder, m.p. $223°$ (decomp.); yield, $2\cdot5$ g. (Found : Cl, $28\cdot8$. $C_{14}H_{13}O_5Cl_3$ requires Cl, $29\cdot0$ per cent.).

The *coumarin* is soluble in acetone, acetic acid and alcohols, but insoluble in benzene, toluene and petrol ether. It dissolves in alkali with deep red colouration, and in conc. H_2SO_4 with yellow colour.

The above condensation was tried in presence of sulphuric acid by keeping it for 3 hours as in case of 4-ethyl-resorcinol. A very poor yield of the coumarin was obtained, which was identical with the above product (Mixed m.p.).

The *acetyl* derivative prepared as usual crystallised from alcohol in silky snow-white flakes, m.p. $177-178°$. (Found : Cl, $21\cdot5$. $C_{20}H_{19}O_8Cl_3$ requires Cl, $21\cdot6$ per cent.).

Further work on the various substituted phenols is being undertaken.

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CHEMICAL INVESTIGATION OF TINOSPORA CORDIFOLIA (MIERS)

By

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TINOSPORA Cordifolia (N. O. Minispermacæ) is a well-known plant grown throughout India. The vernacular names are :—

Gudach (Bitter plant) or Jwar-Nashini (febrifuge) (Sanskrit). Gulawel (Marathi), Galo (Gujarati) and Gurach (Hindi).

This plant is extensively used in Ayurvedic medicine as a febrifuge particularly in malignant fever. Usually a decoction of the stems is prescribed. It is exceedingly bitter. This bitter principle does not seem to have been investigated with any degree of success so far.

Fluckiger reports that the bitter principle is a glucoside and also traces of berberine are found. He was unable to get any crystalline product. (Dymock, Warden and Hooper, Pharm. Indica., Vol. I, page 56). Kirtikar ascribes its medicinal value to be due to traces of berberine. (Indian Medicinal Plants, Kirtikar and Basu, page 49).

Gulawel satwa is a powder obtained from the stems of the plants by crushing and washing with water. This satwa is also a popular medicine and is used as a tonic. We have examined a sample of gulawel satwa kindly supplied by Dhoot-Papeshwar Pharmacy, Panwel (Dist. Bombay), and found it to consist of only starch, thus confirming the earlier observation of Kirtikar (loc. cit.). This satwa is not bitter.

We have carried out a systematic chemical investigation of this plant obtained from the Western Ghats. Our samples were collected from plants reared on the mango tree or on cactus. The extracts of the two samples did not show any difference in the substances obtained by extraction. From the stems of the plants we have isolated the following products :—

(1) Bitter Principle A ($C_{22} H_{34} O_{10}, 5H_2 O$)—m.p. 226–228°C.

(2) Bitter Principle B—   —m.p. 186–188°C.

(3) Dark green oil which appears on preliminary examination to contain glycerides of myristic and palmitic acids.

(4) A neutral substance—a fatty alcohol ($C_{28} H_{58} O$) m.p. 82–83°C.

Isolation of different substances.—The alcoholic extract was cooled. A semi-crystalline mass separated which was filtered off. This semi-crystalline mass gave after several crystallizations from light petroleum *a neutral substance* (m.p. 82–83°C).

The alcoholic filtrate, after the removal of the above neutral substance, was treated with lead acetate and the precipitate removed. The excess of lead was removed by hydrogen sulphide and alcohol was filtered off from the distillate. The residue while still hot was mixed with a small

quantity of water and was shaken with benzene. The aqueous layer on cooling deposited in fine needles a *Bitter Principle A* which after several crystallizations from water melted at 226–228°C. The benzene extract was concentrated and diluted with light petroleum, when silky needles of another *Bitter Principle B* separated, which on recrystallization from methyl alcohol melted at 186–188°C.

Neutral Substance m.p. 82–83 ($C_{28} H_{58} O$). It is quite white and is soluble in all organic solvents in hot and sparingly soluble in cold. Its mol. wt. is 415 and corresponds to C_{28} alcohol. It is characterised by its acetyl derivative prepared in the usual way (m.p. 75°). It gives a blue colour with chloroform and antimony chloride after a day. This alcohol appears to be Octacosanol ($C_{28} H_{58} O$) (Pollard, Chibnall and Piper, J. Biochem., 1931, 27, 1889, and Ulrich and Bluberg, Ber., 1931, 64, 2512).

Bitter Principle A (m.p. 226–228°) is the most important principle and is found to the extent of 0·1 per cent. on the weight of the stems. It can be crystallised from boiling water in lustrous needles and is very soluble in alcohol and insoluble in chloroform petrol or benzene. The crystals contain water of crystallization which can be removed in a desiccator or on a water bath. The melting points of both the hydrated and the anhydrous variety are the same (226–228°C). There is no nitrogen present. The substance is readily acetylated (acetyl derivative m.p. 213–214°C). There is no ethoxy or methoxy group. Tests for aldehydic and ketonic groups were negative. Hydrolysis of the substance with dilute acids gives a dark amorphous material and the solution becomes fluorescent. From the residue no osazone or hydrazone was obtained by the reaction of phenyl-hydrazine. Hydrolysis with bases proceeds smoothly preferably in an atmosphere of hydrogen and an intense blue colouration is obtained. On acidifying an orange coloured precipitate is obtained which can be crystallised from methyl alcohol and had mol. wt. 830, showing that some condensation is going on. The bitter principle (A) (anhydrous) is optically active and has a dextro rotation of 48° in acetone solution.

Bitter Principle B (m.p. 186°C) has a mol. wt. about 475 and can be crystallised from methyl alcohol in clusters of needles; it is insoluble in water, benzene, and petrol and is not a glucoside. This bitter principle is being investigated.

Recently Jois (Proc. Ind. Sci. Congress, 1941) has isolated three different substances from this plant melting at 75–77°C, 83–84°C and 181°C. Jois's substance melting at 83–84°C may be identical with our substance melting at 82–83°C and his substance m.p. 75–77°C may be an impure variety of the same. Similarly his substance (m.p. 181°C) may also be identical with that of our substance melting at 186°C. But Jois has not isolated the bitter principle m.p. 226°C which we get in larger proportion. This difference may be due to the fact that his samples may not have been reared on mango trees. We have found that these bitter principles obtained by us could not be obtained from the plants reared on the neem trees.

Further work is in progress.

<center>EXPERIMENTAL</center>

Extraction with different solvents.—In order to ascertain the general character of the constituents, 100 gms. of the powdered stems of this plant were successively extracted in a soxhlet apparatus with different solvents. The percentage of dry extracts and the nature of the extracts is given in Table I.

<center>*Table I*</center>

Solvent used	Per cent. of extract	Nature of extract
1. Petrol	0·5	Oily and wavy.
2. Ether sulphuric	0 5	Yellowish oil traces of bitter principle A.
3. Chloroform	0 45	Yellowish semi solid.
4. Alcohol	0·15	Yellowish semi solid gives the three different substances given below.

Investigation of the oil.—The oil obtained in the petrol extract was examined in the usual way. But the quanity being small, complete analysis of the oil could not be made. However, it appears that the glycerides of myristic and palmitic acids are present.

EXTRACTION OF THE BITTER PRINCIPLES AND THE NEUTRAL MATTER

Extraction of the bitter principle A.—The powdered stems of the plant are extracted with alcohol till the new extract is no longer bitter. The extract while warm is quite clear but on cooling overnight a considerable quantity of a semi crystalline material (Extract A) separates. This is removed. The filtrate is treated with lead acetate just sufficient to remove the tannins. The lead precipitate is filtered and the filtrate is saturated with hydrogen sulphide to remove small quantities of lead which invariably remain there. The pale yellow coloured filtrate is distilled on a water bath till almost free from alcohol. The residue while still hot is poured into a small quantity of water and quickly shaken with benzene. The benzene layer (Extract B) is removed and the acqueous layer, which contains some black tar, is allowed to stand. Within an hour silky needles make their appearance. The crystals are removed and crystallised from boiling water. It melts at 226–225°C. The crystals lost 16·4 per cent. of water on heating at 100°C. or in a vacuum desiccator. The mol. wt. of the anhydrous substance was determined by Rast's method and was found to be 448 and 458. The combustion of the anhydrous substance gave

C, 57°9 per cent. and H, 7·19 per cent.

$C_{22} H_{34} O_{10}$ requires C, 57·64 per cent.

H, 7·42 per cent. and mol. wt. 458.

The water of crystallization amounts to five molecules of water and hence the formula of the crystalline substance is

$$C_{22} H_{34} O_{10}, 5 H_2 O.$$

The anhydrous substance was dextro rotatory in acetone solution and had

$$\propto_D = 48° \text{ at } 26°C.$$

Methylation of the bitter principle A was tried by silver oxide and methyl iodide and diazomethane. In each case the substance was obtained unchanged. When potassium carbonate was used instead of silver oxide in acetone solution, the substance was decomposed.

Acetyl derivative of bitter principle A was prepared by heating the substance with sodium acetate (anhydrous) and acetic anhydride. It crystallised from dilute alcohol in needles and melts at 213°C.

Extraction of the bitter principle B.—The benzene extract (B) from several extractions is collected together and benzene is removed under reduced pressure. The residue contains an oil, a considerable portion of an amorphous black solid and a bitter substance. To isolate this second bitter principle (B), petrol, b.p. 60–80°C., is added to the black residue when the oil and the black material dissolve and leave a crystalline residue which after crystallization from methyl alcohol melts at 186–188°C. The quantity of this substance is very small (0·01 per cent.) and is being further investigated.

Extraction of the neutral substance.—The semi crystalline extract (A) obtained in the beginning is crystallised from petrol till almost free from the green and yellow colouring matter. The white powder is then extracted with ether in which it is sparingly soluble. This substance is then finally crystallised from low boiling petrol.

(Found C, 81·9 per cent. ; H, 14·26 per cent. ; Mol. wt., 415, 423 by Rast's method.

$C_{28} H_{58} O$ requires C, 81·95 per cent.;

H, 14·14 per cent. and mol. wt., 410).

Acetyl derivative of the neutral matter prepared in the usual way on crystallization from hexane had m.p. 75°C. Acetyl group estimation of the compound showed that it had only one acetyl group.

(Found C, 79·6 per cent., H, 13·3 per cent.

Calc. for $C_{30} H_{60} O_2$; C=79·64 per cent. ; H=13·25 per cent.). This neutral substance, therefore, seems to be octacosenol.

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THE CHEMISTRY OF ALKYLCYCLOPENTANONES, PART IV—THE SYNTHESIS OF 1-CARBOXY-3-METHYL-CYCLOPENTANE-1-∝-BENZYLACETIC, 1-CARBOXYCYCLOPENTANE-1-∝-BENZYLACETIC AND 1-CARBOXY-CYCLOPENTANE1-∝-PROPIONIC ACIDS

By

R. D. DESAI AND G. S. SAHARIYA

IN the course of our study of the cyclohexane derivatives we have synthesised the various 2-methyl, 3-methyl, and 4-methyl-cyclohexane-1-carboxy-1- ∝ -benzylacetic acids (Unpublished work). Each one of the acids exists in two forms only. If this isomerism was explained on the basis of the geometrical isomerism of the uniplanar cyclohexane ring, the same phenomenon should be encountered in the case of 1-carboxy-3-methylcyclopentane-1- ∝ -benzylacetic acid. (I) This was prepared by the acid hydrolysis of ethyl 1-cyano-3-methylcyclopentane-1- ∝ - benzylcyano acetate (II) which was obtained by the benzylation of the dicyano ester (III). The acid exists only in one form showing that the cis-form is not stable enough for isolation. In an attempt to prepare the lower homologue of this acid by the acid hydrolysis of the benzylation product of the dicyanoester obtained by condensing cyclopentanone-cyanohydrin with ethyl sodiocyanooacetate, a monobasic acid having the composition $C_{14}H_{16}O_2$ was encountered. This was proved to be ∝ -benzyl- ∝ -1 : 2-cyclopentenyl-acetic acid (IV) derived from the benzylation of cyclopentylidene cyanoacetate which is known to undergo alkylation in the B-Y-phase (VI) (Kon and Co-workers, J. (1923), *123*, 1369 ; Desai and Sahariya, J. Univ. Bom. (1939), *8*, 239).

Methylation of the dicyanoester obtained from ethylsodiocyano-acetate and cyclopentanone-cyanohydrin followed by the acid hydrolysis gave 1-carboxy-cyclopentane-1- ∝ -propionic acid which was characterised by the anilic and p-toluidinic acids.
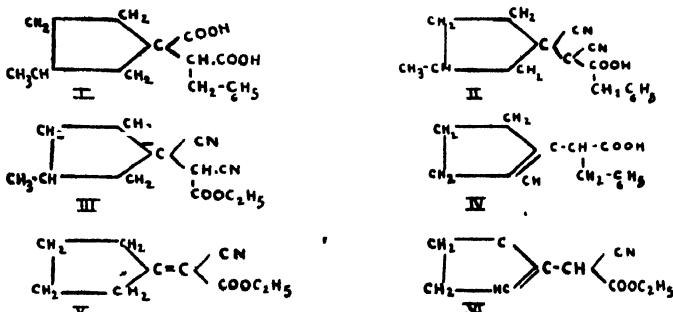
EXPERIMENTAL

Ethyl-1-Cyano-3-methylcyclopentane- ∝ *-benzylcyanoacetate.*—A suspension of ethylsodiocyano-acetate (Na=4˙2g ; cyanoacetate=24g ; ethyl

alcohol 40 cc.) was added to a solution of 3-methyl-cyclo-pentanone-cyanohydrin (22g) in absolute alcohol (20 cc.) with constant stirring and cooling. After allowing the mixture to stand at the ordinary temperature for 48 hours, benzyl chloride (25g) was added " in situ " in three lots, cooled, kept at the ordinary temperature for two days, and heated under reflux till the mixture was neutral. After distilling off as much of alcohol as possible, the oil precipitated on diluting the residue with water was extracted with ether, dried and distilled under reduced pressure. Three fractions were collected (1) B. P. 90–120 30 mm. (2) B. P. 120–200/30 mm. (3) B. P. 240–250/30 mm. The first fraction was rejected, while the second fraction was again treated with benzyl chloride in presence of sodium ethoxide. Total yield of ethyl 1-cyano-3-methylcyclopentane-1- ∝ -benzyl-acetate boiling at 252–254/30 mm. was 60 per cent. and was a viscous liquid.

(Found C, 73·2; H, 7·2. C_{19} H_{22} O_2 N_2 requires C, 73·5; H, 7·1 per cent.).

Hydrolysis of the Ester to 1-Carboxy-3-methyl Cyclopentane-1- ∝ - benzylacetic acid.—The ester (20g) which was dissolved in concentrated sulphuric acid (30 cc.) and kept overnight was diluted with water (40 cc.) and the mixture heated under reflux on sand-bath for 20 hours. The cooled mixture was diluted with water, saturated with ammonium sulphate, extracted with ether and purified through sodium carbonate. As the acid did not solidify, it was suspected to contain 1-carboxy-3-methyl-cyclopentane-1-acetic acid. The gummy mixture of the acids was converted into a mixture of calcium salts through the ammonium salt, and calcium chloride. The insoluble calcium salt was removed, while the soluble calcium salt, on acidification with hydrochloric acid gave an acid which was extracted with ether. This acid which solidified after some time in a vacuum was triturated with benzene, and finally crystallised from a mixture of benzene and hexane when white, rectangular plates mp. 112° were obtained.

(Found C, 70·0; H, 7·5. C_{16} H_{20} O_4 requires C, 69·6; H, 7·2).

Its anhydride is a liquid while its lead and copper salts are insoluble in cold as well as hot water, but the calcium and barium salts are soluble.

Preparation of Ethyl 1-Cyano-Cyclopentane-1- ∝ -benzyl-cyanoacetate.— This was prepared from cyclopentanone-cyanohydrin=(20g) ethyl sodiocyano-acetate (Na=4·6g; ethyl cyanoacetate 24g; absolute alcohol=50 cc.) and benzyl chloride (24 cc.) in the usual manner. The reaction product was separated into three fractions by distillation under reduced pressure. (1) b. p. 90–110/15 mm. (2) b. p. 110–200/15 mm. (3) b. p. 220–225/15 mm. which solidified on cooling to a hard, crystalline mass and crystallised from dilute alcohol in long rectangular plates m.p. 70°. (Yield=45 per cent.)

(Found C, 72·6; H, 6·7. C_{18} H_{20} O_2 N_2 requires C, 72·9; H, 6·7 per cent.).

Hydrolysis of the Ester to 1-Carboxy-cyclo-pentane-1- ∝ -benzylacetic acid.—A solution of the ester (10g) in concentrated sulphuric acid (20 cc.)

which had been kept for 12 hours was diluted with water (20 cc.) and heated on sand-bath under reflux for 24 hours. The acid, isolated in the usual manner, was purified through alkali, and triturated with benzene when a solid m.p. 138–140° was obtained. The *acid* crystallised from hot benzene in white, small plates m.p. 145°. It is soluble in alcohol, acetic acid, acetone and chloroform, but very sparingly soluble in benzene and petrol. Its calcium and barium salts are soluble, while the lead and copper salts are insoluble in hot water.

(Found C, 68·9 ; H, 6·7. $C_{15} H_{18} O_4$ requires C, 68·7 ; H, 6·9).

The anhydride obtained by heating the dry acid (0·5g) in a tube at 170° for three hours crystallised from hexane in lustrous laminx m.p. 115°.

(Found C, 73·5 ; H, 6·5 $C_{15} H_{16} O_3$ requires C, 73·8 ; H, 6·6 per cent.).

The anilic acid prepared in benzene solution was soluble in this solvent. The solid left after the removal of the solvent was extracted with a solution of sodium bicarbonate, and the alkaline solution acidified. It crystallised from dilute alcohol in plates m.p. 159–160°.

(Found C, 74·5 ; H, 6·9 $C_{21} H_{23} O_3$ N requires C, 74·8 ; H, 6·8 per cent.).

Δ—1 : *2-Cyclopentenyl-* ∝ *-benzylcyanoacetate.*—Benzylchloride (12·6g) was slowly added to a solution of cyclopentylidenecyano-acetate (18g) in sodium ethoxide (2·3Na ; alcohol—45 cc.) and the mixture heated on water bath for 6 hours. The oil precipitated on pouring the mixture into water was extracted with ether, dried, recovered and distilled when the liquid b. p. 234–235/16 mm. was obtained (Yield=11gms.).

(Found C, 75·4 ; H, 7·0 $C_{17} H_{19} O_2$ N requires C, 75·8, H, 7·1 per cent.).

Hydrolysis of the Ester to Δ—1 : *2-Cyclopentenyl-* ∝ *-benzyl-acetic acid.*—The ester (10g) dissolved in concentrated sulphuric acid (20 cc.) was kept overnight and diluted with water (20 cc.). The mixture was heated on sand-bath under reflux for 12 hours, and the acid isolated and purified in the usual manner was crystallised from dilute alcohol when white needles m.p. 156–157° were obtained.

(Found C, 74·4 ; H, 6·9 equiv.=228. $C_{14} H_{16} O_2$ ½ H_2O requires C, 74·7 ; H, 7·1 per cent. equiv.=225).

The acid is soluble in the usual organic solvents, but sparingly soluble in petrol. Its lead and copper salts are insoluble in cold as well as hot water, while the calcium and barium salts are soluble.

Methylation of Ethyl 1-Cyanocyclopentane-1-cyanoacetate and formation of Ethyl 1-Cyano-cyclopentane-1- ∝ *-Cyano-propionate.*—To the suspension of ethyl sodio-1-cyanocyclopentane-1-cyano-acetate formed by the addition of ethyl sodio cyano-acetate (Na=2·3g abs. alcohol=40 cc. cyanoacetic ester 14g) to cyclopentanone-cyanohydrin (12g) dissolved

in absolute alcohol (15 cc.), methyl iodide (16g) was gradually added in situ, and the mixture was allowed to stand at the room temperature for 48 hours. The mixture which become neutral after warming on the water-bath under reflux for 16 hours was poured into water after the removal of as much alcohol as possible. The precipitated oil was extracted with ether, dried, recovered, and distilled under reduced pressure. The first fraction b. p. 90–120°/14 mm. was rejected, while the second fraction (12g) boiling b. p. 140–180°/14 mm. was remethylated on the supposition that one-third of it was unmethylated. The pure *Ethyl 1-cyano-cyclopentane-1- ∝ -cyanopropionate* boiled at 152–154°/10 mm. (Yield=10 gms.). There was some undistillable product which was not examined.

(Found C, 65·2 ; H, 7·1 $C_{12} H_{16} O_2 N_2$ required C, 65·4 ; H, 7·3 per cent.).

Hydrolysis of the Ester to 1-Carboxy-Cyclopentane-1- ∝ -propionic acid.— The ester (10g) was hydrolysed as usual with 66 per cent. sulphuric acid (50 cc.) by heating on sand-bath under reflux for 24 hours. The crude acid crystallised from dilute alcohol in plates mp. 140°.

(Found C, 57·8 ; H, 7·5 $C_{19} H_{14} O_4$ require C, 58·0 ; H, 7·5 per cent.).

Its lead salt is insoluble in hot as well as cold water while the copper, calcium and barium salts are soluble.

The Anhydride was a liquid and was not analysed. *The Anilic acid* crystallised from dilute alcohol in white needles m.p. 170°.

(Found C, 69·1 ; H, 7·4 $C_{15} H_{19} O_3 N$ requires C, 69·0 ; H, 7·3 per cent.).

The p-Toluidinic acid crystallised from dilute alcohol in colourless needles m.p. 167°.

(Found C, 69·7 ; H, 7·6 $C_{16} H_{21} O_3 N$ requires C, 69·8 ; H, 7·6 per cent.).

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THE CONDENSATION OF SUCCINIC ANHYDRIDE WITH RESORCINOL AND ORCINOL

Another Case of γ-substitution in Orcinol

By

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SUCCINIC anhydride has already been condensed with aromatic hydrocarbons and phenolic ethers so as to obtain β-benzoyl-propionic acid and its derivatives. Phenol and its homologues have also been condensed with phthalic anhydride [Ullmann and Schmidt, Ber. (1919), 52, 2098 ; Ullmann and Conzetti, ibid, 1920, 53, 830] and with succinic anhydride [Mitter and De, J. Ind. Chem. Soc. (1935), 12, 747 ; Raval, Bokil and Nargund, J. Univ. Bom. (1938), 7, 184]. Dihydric phenols have not at all been condensed with succinic anhydride, while Dalal and Nargund [J. Univ. Bom. (1938), 7, 189] have reported their failure to condense resorcinol with this anhydride.

Our main objective in studying this reaction was to see whether β-dihydroxy-benzoyl-propionic acids could be prepared directly or not. Secondly we wanted to know whether the γ-substitution which had been observed by Desai and Co-workers [Proc. Ind. Acad. Sci. (1938), 8, 200 ; (1940), 12, 391] in the case of the Friedel-crafts Reaction between acid chlorides and resorcinol derivatives would take place in this case also. With these objects in view we condensed resorcinol, orcinol, resacetophenone, β-methyl-resorcylate, ∝-naphthol and phloroglucinol with succinic anhydride in the presence of anhydrous aluminium chloride. A good yield of β-2 : 4-dihydroxy-benzoyl-propionic acid (I) was readily obtained from resorcinal and succinic anhydride, while the yield of β-2 : 6-dihydroxy-4-methylbenzoyl-propionie acid (II) from orcinol was fairly poor. These two acids have been characterised by their 4-nitrophenyl hydrazones. Their constitutions were determined by oxidising them with alkaline hypobromite when β-resorcylic and p-orsellinic acids were obtained, showing that orcinol underwent γ-substitution.

Our attempts to condense resacetophenone, β-methyl resorcylate, phloroglucinol and ∝-naphthol with succinic anhydride either in the presence of anhydrous aluminium chloride or zinc chloride and using nitrobenzene and acetylene tetrachloride as solvents were not successful. We were also unsuccessful in condensing the chloride of succinic acid ester with resacetophenone, and β-methyl resorcylate in the presence of alcl$_3$ or Zncl$_2$. The work is being continued with other anhydrides.
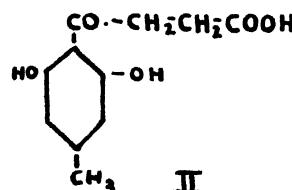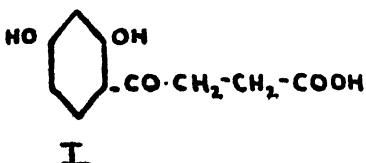
Experimental

β-2 : 4-dihydroxybenzoyl-propionic acid.—To a solution of resorcinol (11g) and anhydrous aluminium chloride (27g) in nitrobenzene (150cc.), succinic anhydride (10g) was slowly added and the mixture was heated in water-bath for one hour after keeping at the ordinary temperature for 48 hours. Having decomposed the aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was distilled off in steam. The solid that separated out on the addition of sodium chloride to the solution was filtered off, and the filtrate gave more solid on extracting with ether. The crude acid which was purified through sodium bicarbonate was crystallised from dilute alcohol in plates m.p. 199–200°. Its alcoholic solution gave brownish red colouration with ferric chloride. (Yield= 40 per cent.).

(Found C, 57·2 ; H, 4·9. $C_{10}H_{10}O_5$ requires C, 57·0 ; H, 4·8 per cent.).

The p-nitrophenylhydrazone was prepared by heating the alcoholic solution of the Keto-acid (0·4g) with p-nitrophenylhydrazine (0·3g) for 6 hours, and crystallised from the solvent in small, red needles m.p. 194° (dec.).

(Found N, 11·8 ; $C_{16}H_{15}O_6N_3$ requires N, 12·2 per cent.).

Oxidation of the Keto-acid to β-resorcylic acid.—The acid (0·5g) dissolved in 5 per cent. NaoH (20cc.) was slowly oxidised with 2 per cent. sodium hypobromite solution (25cc). After acidification with hydrochloric acid, the solution, on extraction with ether, gave an acid which was identified as β-resorcylic acid by m.p. and mixed m.p. with an authentic specimen.

β-2 : 6-dihydroxy-4-methyl-benzoyl-propionic acid was similarly prepared from anhydrous orcinol (12·5g), succinic anhydride (10g) and aluminium chloride (27g). The cold solution obtained after the removal of nitro-benzene deposited a solid which after purification through sodium bicarbonate crystallised from dilute alcohol in colourless needles m.p. 207°. Its alcoholic solution gave a dark-green colouration with ferric chloride. (Yield = 8 per cent.).

(Found C, 58·6 ; H, 5·5. $C_{11}H_{12}O_5$ requires C, 58·9 ; H, 5·4 per cent.).

The Keto-acid gave p-orsellinic acid on oxidation. The filtrate from the original solution was extracted with ether after saturation with sodium chloride. A viscous oil was obtained, and this gave orcinol on extraction with benzene.

The p-nitrophenylhydrazone was prepared in the usual manner and crystallised from alcohol in small, red crystals m.p. 203–204° (dec.).

(Found N, 11·3 ; $C_{17}H_{17}O_6N_3$ requires N, 11·7 per cent.).

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SYNTHETICAL ANTHELMINTICS—PART II

γ-substituted butyrolactones

By

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ROSENMUND and Schapiro (Arch. Pharm. 1934, *272*, 313) prepared a number of γ-substituted butyrolactones with a phenyl group having a hydroxyl, methoxyl or methyl group as a substituent on γ-carbon atom. It was found that γ-p-methoxyphenyl-butyrolactone had thrice the anthelmintic properties of santonine. The present work is an attempt in the same direction, γ-substituted butyrolactones, not previously reported by Rosenmund and Schapiro are now prepared and described in the following pages.

The method adopted for the preparation of lactones was to reduce a substituted γ-keto butyric acid with sodium and alcohol, followed by lactonising the hydroxy acid by boiling with dilute sulphuric acid. The keto buyric acids were prepared by Friedel and Craft's reaction of succinic anhydride on phenol or phenol methyl ether.

EXPERIMENTAL

γ-o-methoxy-phenyl-butyrolactone

ß-o-methoxy-benzoyl-propionic acid.—It was prepared by methylating (by dimethyl sulphate and ten per cent. solution of sodium hydroxide) β-o-hydroxy-benzoyl-propionic acid of Raval, Bokil and Nargund (Jour. Bom. Univ., 1938, *VII*, Part 3, page 184). It was soluble in alcohol, chloroform, acetic acid, ethyl acetate and benzene but insoluble in petrol and water. It was crystallised from benzene petrol mixture in prisms m.p. 98°. Barium and calcium salts of this acid were soluble in water and the silver salt was soluble in hot water. (Found : C, 63·6 ; H, 6·1 per cent. ; Eq. wt., 207·2. Ag in silver salt, 35·0 per cent. $C_{11} H_{12} O_4$ requires C, 63·5 ; H, 5·8 per cent. ; Eq. wt., 208. $C_{11}H_{11}P_4Ag$ requires Ag, 34·3 per cent.). *Methyl-ß-o-methoxy-benzoyl-propionate* prepared by Fischer Speier method had b.p. 160° at 3 mm. D_4 $^{27·5}$=1·168 N_D $^{27·5}$=1·5278. (Found : C, 64·7 ; H, 6·5 per cent. $C_{12} H_{14} O_4$ requires C, 64·9 ; H, 6·3 per cent.). *Ethyl β-o-methoxy-benzoyl propionate* prepared similarly had b.p. 170° at 7 mm. D_4 $^{27·5}$=1·134 N_D $^{27·5}$=1·5189 (Found : C, 66·3 ; H, 6·9 per cent. $C_{13} H_{16} O_4$ requires C, 66·1 ; H, 6·8 per cent.). *Reduction of β-o-methoxy-benzoyl-propionic acid.*—The acid (10 gms.) was dissolved in absolute alcohol (100 cc.) and heated in oil bath to 100°. Sodium (10 gms.) was then added in one lot and heating continued till the whole of it dissolved. It was cooled,

decomposed with water and extracted with ether to remove neutral impurities. It was then acidified with sulphuric acid and more of the latter added till the concentration of sulphuric acid came to about 15 per cent. It was boiled for two hours, cooled, extracted with ether and the recovered substance was left over a saturated solution of sodium bicarbonate for 24 hours. The lactone was then extracted with ether, dried and ether removed. γ-o-methoxy-phenyl-butyrolactone thus obtained had b.p. 170° at 16 mm. (Found : C, 69·0; H, 6·4 per cent.; Eq. wt., by back titration, 188. $C_{11} H_{12} O_3$ requires C, 68·8; H, 6·3 per cent.; Eq. wt., 192).

γ-2-methoxy-4-tolyl-butyrolactone

β-2-methoxy-4-toluoyl-propionic acid.—It was prepared by methylating β-2-hydroxy-4-toluoyl-propionic acid of Raval, Bokil and Nargund (loc. cit). It was soluble in alcohol, chloroform, acetic acid, ethyl acetate and sparingly soluble in benzene but insoluble in petrol. It crystallised in needles from benzene m.p. 126°. Calcium salt was soluble while barium and zinc salts were insoluble. (Found : C, 65·2; H, 6·5 per cent.; Eq. wt., 220. $C_{12} H_{14} O_4$ requires C, 64·9; H, 6·3 per cent.; Eq. wt., 222). *Methyl-β-2-methoxy-4-toluoyl-propionate* was a colourless liquid b.p. 190–192° at 14 mm. $D_4^{29·5} = 1·142$. $N_D^{29·5} = 1·5300$. (Found : C, 66·4; H, 7·0 per cent. $C_{13} H_{16} O_4$ requires C, 66·1; H, 6·8 per cent.). *Ethyl-β-2-methoxy-4-toluoyl-propionate* was a colourless solid soluble in the usual solvents. It crystallised from hot petrol or alcohol in needles m.p. 76°. (Found : C, 67·3; H, 7·5 per cent. $C_{14} H_{18} O_4$ requires C, 67·2; H, 7·2 per cent.). *γ-2-methoxy-4-tolyl-butyrolactone* prepared by reduction with sodium and alcohol and worked up as described before was a colourless liquid b.p. 197–198° at 9 mm. $D_4^{1·5} = 1·071$ $N^{36·5} = 1·5309$. (Found : C, 70·3; H, 7·0 per cent. $C_{12} H_{14} O_3$ requires C, 69·9; H, 6·8 per cent.). *γ-2-methoxy-4-tolyl-γ-hydroxy-butyric acid* prepared from the above lactone by dissolving in hot alkali and then neutralising in cold with the requisite quantity of dilute sulphuric acid, was a colourless solid crystallising from benzene in rectangular plates m.p. 114°. (Found : C, 64·2; H, 7·4 per cent.; Eq. wt., 223·7. $C_{12} H_{15} O_4$ requires C, 64·3; H, 7·1 per cent. Eq. wt., 224).

γ-3 : 4-dimethoxy-phenyl-butyrolactone.—It was obtained by reduction of 3 : 4-dimethoxy-benzoyl-propionic acid of Dalal and Nargund (Jour. Ind. Chem. Soc., 1937, 406). It was a colourless solid soluble in the common solvents except alcohol in which it was sparingly soluble. It crystallised in thin plates from alcohol or benzene petrol mixture m.p. 120–121°. (Found : C, 65·1; H, 6·5 per cent. Eq. wt., by back titration, 218. $C_{12} H_{14} O_4$ requires C, 64·9; H, 6·3 per cent. Eq. wt., 222).

γ-2 : 5-*dimethoxy-phenyl-butyrolactone.*—It was obtained by the reduction of β-2 : 5 dimethoxy-benzoyl-propionic acid of Dalal and Nargund (loc. cit). It was sparingly soluble in hot alcohol and soluble in all other solvents except petrol. It crystallised in needles from alcohol m.p. 94–95°. (Found : C, 64·8 ; H, 6·4 per cent. Eq. wt., by back titration, 219·3. $C_{12} H_{14} O_4$ requires C, 64·9 ; H, 6·3 per cent. Eq. wt., 222).

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SYNTHETICAL ANTHELMINTICS—PART III

γ-γ-disubstituted butyrolactones

By

J. J. TRIVEDI AND K. S. NARGUND

ROSENMUND and Schapiro (Arch. Pharm. 1934, *272*, 313) showed that γ-p-methoxy-phenyl-butyrolactone was thrice as effective on living ascarids as santonine. It is a recognised fact that an alkyl substituent in phenols so modifier the antiseptic properties as to render them valuable internal antiseptics, the well known example being that of hexyl-resorcinol. We, therefore, thought of introducing an additional alkyl group in γ-p-methoxy-phenyl-butyrolactone with a view to enhance its anthelmintic properties. The present communication deals with γ-alkyl-γ-p-methoxy-phenyl-butyrolactones. For the sake of comparison γ-alkyl-γ-phenyl-butyrolactones are also prepared and described in the present paper.

The action of grignard reagent on a keto ester was first investigated by Grignard (Comp. Rend. 1902, *135*, 629) who showed that the keto group reacted with the reagent in preference to the ester group provided molecular proportions of both are used. Similar results were obtained by Jones and Tattersall (J. C. S. 1904, *85*, 1691) and Noyes and Marvel (J. A. C. S. 1917, *39*, 1267). Porter (J. A. C. S. 1923, *45*, 1086) tried the action of the grignard reagent on a keto acid and showed that the result was similar to that of a keto ester. We have now tried the action of grignard reagents on ethyl β-benzoyl propionate and ethyl β-p-methoxy-benzoyl propionate in molecular proportions and found that γ-alkyl-γ-phenyl-butyrolactones and γ-alkyl-γ-p-methoxy-phenyl-butyrolactones could be prepared in good yields. The use of the free keto acid in the above reaction was found to be quite unsatisfactory.

The compounds described in this and in the preceding paper are being tested for anthelmintic properties and the results will be communicated in due course.

EXPERIMENTAL

Ethyl-β-benzoyl-propionate was prepared from β benzoyl propionic acid by Fischer Speier method. It had b.p. 203 at 60 mm. Kugel (Ann. *299*, 62) gives the b.p. of this ester as 192° at 33 mm.

Ethyl-β-p-methoxy-benzoyl-propionate.—It was similarly prepared from β-p-methoxy-benzoyl-propionic acid of Rosenmund and Schapiro (loc. cit.). It was a colourless solid, soluble in the common solvents but insoluble in petrol. It crystallised from dilute alcohol or benzene petrol mixture in long needles m.p. 57°. (Found : C, 66·3 ; H, 6·9 per cent. $C_{13}H_{16}O_4$ requires C, 66·1 ; H, 6·8 per cent.).

General procedure for the action of grignard reagents on keto esters :—
To a solution of the keto ester (0·075 mol) in dry ether (50 cc.) cooled
in ice bath, was added drop by drop the grignard reagent prepared from
alkyl bromide (0·075 mol) magnesium (2 gms) and dry ether (50 cc.).
The flask was kept well shaken during addition of the reagent. The
complex formed usually separated as greenish mass. It was left at ordinary
temperature for half an hour, decomposed with ice and sulphuric acid
and the product, recovered by ether extraction, was directly hydrolysed
by heating with ten per cent. aqueous alcoholic sodium hydroxide solution
on water bath for two hours. After removing alcohol it was extracted
with ether to remove the neutral impurities. It was acidified with dilute
sulphuric acid and more of the latter added till its concentration was about
15 per cent. It was heated on water bath for two hours and the product,
recovered by ether, was left over a saturated solution of sodium bicarbonate
for 24 hours. The lactone was then extracted with ether, dried over
anhydrous calcium chloride, ether removed and the residue purified by
crystallisation if solid or by distillation under reduced pressure if liquid.
The yields of pure lactones were about 40 per cent. Neutral substances
formed in the above reaction have not been investigated. The compounds
are described in tabular forms for the sake of brevity.

Name of the Compound	Formula	Analysis		
		Properties	Found	Required for
γ-Methyl-γ-phenyl-butyrolactone	$C_{11}H_{12}O_2$	Colourless liquid b.p. 145-147° at 5 mm. $N_D{}^{32·5}=1·5273$	C, 74·8; H, 7·0	C, 75·0; H, 6·9.
γ-Methyl-γ-phenyl-γ-hydroxy butyric acid	$C_{11}H_{14}O_3$	Obtained by neutralising in cold an alkaline solution of the above lectone. Short needles from benzene m.p. 106	C, 68·4; H, 7·4	C, 68·1; H, 7·2.
γ-Ethyl-γ-phenyl-butyrolactone	$C_{12}H_{14}O_2$	Colourless liquid b.p. 160° at 10 mm. $D_4{}^{32}=1·092$ $N_D{}^{32}=1·5225$.	C, 76·1; H, 7·4	C, 75·8; H 7·4.
γ-Ethyl-γ-phenyl-γ-hydroxy butyric acid	$C_{12}H_{16}O_3$	Rectangular plates or leaves from benzene petrol, mixture m.p. 102-103°.	C, 69·1; H, 8·0	C, 69·2; H, 7·7.
γ-n-Propyl-γ-phenyl butyrolactone	$C_{13}H_{16}O_2$	Colourless liquid b.p. 145-150° at 20 mm. $D_4{}^{32}=1·077$ $N_D{}^{32}=1·5205$.	C, 76·8; H, 8·2	C, 76·5; H, 7·8.
γ-n-Butyl-γ-phenyl butyrolactone	$C_{14}H_{18}O_2$	Liquid b.p. 173-174° at 10 mm.	C, 77·0; H, 8·2	C, 77·1; H. 8·3.
γ-γ-Diphenyl-butyrolactone	$C_{16}H_{14}O_2$	Colourless solid soluble in the common solvents in hot, prisms for ethyl alcohol. m.p. 90-91°.	C, 81·1; H, 6·0	C, 80·7; H, 5·9.
γ-γ-Diphenyl-γ-hydroxy butyric acid	$C_{16}H_{16}O_3$	Colurless solid prisms or plates from methyl Alcohol m.p. 141°	C, 75·2; H, 6·4	C, 75·0; H 6·3.
γ-p-Methoxy-phenyl γ methyl buty-rolactone.	$C_{12}H_{14}O_3$	Colourless liquid. b.p. 215-220° at 42 mm. partially solidifes on standing.	C, 70·3; H, 6·9	C, 69·9; H, 6·8.
γ-p-Methoxy-phenyl γ methyl γ hydroxy butyric acid.	$C_{12}H_{16}O_4$	Solid soluble in the common solvents except $CHCl_3$ and petrol. Plates from benzene m.p. 120°.	C, 64·1; H, 7·1	C, 64·3; H, 7·1

γ-p-Methoxy-phenyl γ ethyl butyrolactone..	$C_{13}H_{16}O_3$	.. Liquid b.p. 180-185° at 5 mm. $N_D^{31.6}=$ 1·5284.	C, 71·1; H, 7·4	.. C, 70·9; H, 7·3.
γ-p-Methoxy-phenyl γ ethyl γ hydroxy-butyric acid.	$C_{13}H_{18}O_4$	.. Solid soluble in all solvents except petrol. Prisms from benzene m.p. 123°.	C, 65·8; H, 7·7.	..C, 65·5; H, 7·6.
γ-p-Methoxy-phenyl γ n-propyl buty-rolactone.	$C_{14}H_{18}O_3$	.. Liquid b.p. 215-217 at 20 mm. $N_D^{31}=$ 1·5273.	C, 72·1; H, 7·9	.. C, 71·8; H, 7·7.
γ-p-Methoxy-phenyl γ isopropyl butyro lactone.	$C_{14}H_{18}O_3$	.. Liquid b.p. 190° at 12 mm.	C, 72·2; H, 7·7	.. C, 71·8; H, 7·7.
γ-p-Methoxy-phenyl γ n-butyl butyro-lactone.	$C_{15}H_{20}O_3$	.. Liquid b.p. 220-225° at 15 mm. $D_4^{30}=1·070$ $N_D^{30}=1·5222$.	C, 72·9; H, 8·3	.. C, 72·6; H, 8·1.
γ-p-Methoxy-phenyl γ isobutyl butyro-lactone.	$C_{15}H_{20}O_3$	.. Liquid b.p 200-205° at 22 mm.	C, 72·5; H, 8·2	.. C, 72·6; H, 8·1.
γ-p-Methoxy-phenyl γ isoamyl butyro-lactone.	$C_{16}H_{22}O_3$	.. Liquid b.p. 205-210° at 15 mm. $D_4^{26.5}=1·068$ $N_D^{28.5}=1·5199$.	C, 73·5; H, 8 5	.. C, 73·3; H, 8·4.
γ-p-Methoxy-phenyl γ n-hexyl butyro-lactone.	$C_{17}H_{24}O_3$	..Liquid b.p. 215-220° at 7 mm. $D_4 35 =1·048$ $N_D^5=1 5174$.	C, 74·0; H, 8·8	.. C, 73·9; H, 8·7.

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SYNTHETIC PRODUCTION OF CAMPHOR FROM PINENE—PART III

Borneol, Iso-borneol and their Esters

By `

B. G. S. Acharya, R. C. Shah and T. S. Wheeler

IN Parts I and II (Acharya and Wheeler, J. Univ. Bom. *3*, Part II, 1934, 163 and *4*, Part II, 1935, 118), it was not possible to deal fully with the borneols and their esters. As isoborneol is of industrial importance the present paper deals with a large volume of experimental data obtained on the subject. Reference should also be made in this connection to our paper on the synthetic production of terpineol from pinene (Acharya and Wheeler, J. Bom. Univ. *6*, Part II, 1937, 134).

The production of borneol or Iso-borneol directly from pinene or pinene hydrochloride through the intermediate formation of esters is not a smooth reaction. In spite of an extensive literature on the subject no method that can well be used in manufacture has been achieved. It should be noted in this connection that iso-bornyl esters are obtained from camphene and pinene hydrochloride while pinene directly yields bornyl esters. The esters are obtained by treatment of pinene, pinene hydrochloride or camphene with various organic acids. It is then purified and hydrolysed to yield borneol or isoborneol. The low yields of borneols prepared of these esters from pinene and pinene hydrochloride is due to the fact that these esters are impure containing other substances and the borneols obtained on hydrolysis are also impure.

From the researches of Reisman (Bull. Soc. Chim. 1927 (IV), *41*, 94 ; compare Lafont, ibid. 1888 (ii), *49*, 323 ; Delepine, Reisman and Suan, ibid. 1930 (IV), *47*, 966), anhydrous formic acid on pinene yields a mixture of limonene, dipentene, terpinene, terpinolene, diterpenes, terpinyl formate and bornyl formate. With acetic acid also similar results could be obtained, but according to Bouchardat and Lafont (Compt. rend. 1898, *126*, 755 ; Zietsch;l, G. P. 204163 ; G. P. 67255), terpinyl acetate can be made the main product. Various trials by the authors showed however that this was not the case and as usual a mixture was obtained.

PINENE TO ESTERS AND BORNEOL

Use of fatty acids.—The fatty acids gave unsatisfactory results. With acetic acid systematic experiments were made under varying conditions and a summary of the results is given (see Table I). The other acids employed were formic, propionic, butyric, stearic, palmatic, oleic, and trichloro-and monochloro-acetic acids.

Other acids.—Experiments with salicylic and oxalic acids are described. Experiments were also made with benzoic, picric, citric, tartaric, phthalic sulphuric and carbolic acids. But they gave no promising result. Of all the acids which are said to be used on a commercial scale, salicylic is the best. Tetra-chlorophthalic acid (Plant at Vaugouin) though claimed as in commercial use did not give a good result.

In each experiment after completion of the reaction, excess of acid was neutralised with aqueous sodium carbonate. The non-aqueous layer after drying over $CaCl_2$ was fractionated, under reduced pressure to yield the ester. The b. p's. of the various esters as recorded in literature are given in the following table.

Bornyl ester	Acetate	Formate	Propionate	Butyrate	Salicylate	Hydrogen Oxalate
B. P. °C at mm.	$98\text{--}99_{15}$	$95\text{--}105_{10}$	$109\text{--}110_{10\text{-}11}$	$120\text{--}121_{10\text{-}11}$	$171\text{--}173_{5}$	$157\text{--}160_{680}$

The following table shows the maximum yield of borneol for each acid specified :—

Experiment No.	Acid used	Conditions	Percentage yield of borneol	Remarks
1	Acetic	Heated with gl. acetic acid, acetic anyhydride and boric acid.	7·2	
2	Formic	Formic Acid and sodium formate, $ZnCl_2$ as condensing agent 2 per cent	7	
3	Propionic	Sodium propionate and $ZnCl_2$.	9	
4	Butyric	$ZnCl_2$, 2 per cent.	9	
5	Stearic			
6	Palmatic	....	....	Unsuccessful.
7	Oleic			
8	Salicylic	Temp. 100–110° for 60 hrs. and operation repeated.	18	Salicylic acid is the best.
9	Oxalic	CCl_4 as solvent. $FeCl_3$ as catalyst.	18	

Experiment No.	Acid used	Conditions	Percentage yield of borneol	Remarks
10	Phthalic ..	CH$_3$ COONa, 2 per cent.	10	
11	Tetrachlorophthal 1 c acetone as solvent		11	
12	Benzoic ..		.	
13	Picric ..			
14	Citric ..			
15	Tartaric ..	....	....	Unsatisfactory.
16	Sulphuric ..			
17	Carbolic ..			

Use of Acetic Acid

Pinene was heated with glacial acetic acid at ordinary and increased pressure with and without condensing agents and catalysts. The resulting mixture after the removal of unchanged acetic acid by sq. sodium carbonate was dried over CaCl$_2$ and the product was hydrolysed by 50 per cent. aq. caustic soda using 2 gm. mol of base per gm. mol of ester. Borneol was formed only in very small quantities.

In the sealed tube experiments there was a large formation of a mixed product boiling at the ester temperature. This on hydrolysis gave little of borneol.

The results are tabulated below :—

Pinene   Bornyl acetate (atmos. pr.)

Pinene and gl. acetic acid (2 mols) were refluxed for 18–24 hours

Experiment No	Experiment	Percentage yield of borneol	Remarks
1	No condensing agent used		No result.
2	H$_2$SO$_4$ (4 per cent.) as condensing agent ..	9·7	
3	Excess of CH$_3$COOH		No result.
4	Excess of 4 per cent. H$_2$SO$_4$	10	
5	Used other condensing agents like CH$_3$COONa, ZnCl$_2$		No results.
6	Used acetic anhydride		No result.
7	Pinene, boric acid, acetic anhydride refluxed ..	7·2	

PINENE BORNYL ACETATE
(Sealed tube experiments) Acid 2 mols, Pinene 1 mol

Experiment No.	Condensing Agent	Temp. in °C	Percentage yield of "esters"	Percentage yield of borneol	Remarks
1	Nil	125–135	51·1	2	
2	4 per cent. H₂SO₄ / 6 per cent. water	125–135	55·5	2·1	
3	8 per cent. H₂SO₄ / 10 per cent. water	125–135	52·7	2	
4	16 per cent. H₂SO₄ / 24 per cent H₂O	125–135	56·4	2·5	The "ester" product is in all cases a mixture.
5	16 per cent. H₂SO₄ / 28 per cent. H₂O	125–135	45	2	
6	4 per cent. H₂SO₄	125–135	40	3·2	
7	8 per cent. H₂SO₄	125–135	45	3·5	
8	12 per cent. H₂SO₄	125–135	44·5	3	
9	8 per cent. H₂SO₄ / 12 per cent. H₂O	135–140	55	2·2	
10	4 per cent. H₂SO₄ / 6 per cent water.	135–140	50	2	
11	1 mol acid and 40 per cent. H₂O, 4 per cent. H₂SO₄	125–135	45	Nil.	The "ester" product is in all cases a mixture.
12	4 per cent. CH₃COONa	125–135	58	3·3	
13	8 per cent. CH₃COONa	125–135	50	3	
14	4 per cent. ZnCl₂	125–135	50	3·5	
15	8 per cent. ZnCl₂	125–135	48	2·5	

Use of oxalic acid.—As there is a large amount of patent literature a number of systematic experiments was made on the action of oxalic acid on pinene but yielded no useful result.

The use of metallic oxalates alone, or in conjunction with oxalic acid have not so far been tried. Some experiments were made, but gave no better result. The reaction was also tried using catalysts like V_2O_5, Al_2O_3, China Clay, sand, pyridine, H_2SO_4, $ZnCl_2$, CH_3COONa. The use of solvents has been studied thoroughly by previous workers.

An equimolecular mixture of pinene and oxalic acid was employed unless otherwise stated, as it gave the best result in a series of experiments made to try the proportions.

After the reaction the unchanged oxalic acid is removed by shaking with hot water, and the whole is washed with aq. alkali. The resulting non-aqueous product after drying over $CaCl_2$ is distilled under reduced

pressure to remove unacted pinene and the residue fractionated to obtain the esters bornyl hydrogen oxalate and bornyl oxalate. These were saponified with aqueous caustic soda. Aqueous potash did not improve the hydrolysis yield.

The best yield of borneol obtained by the use of oxalic acid and pinene is 18 per cent. This yield is obtained by refluxing equimolecular proportions of pinene and oxalic acid (anhydrous) with twice the Vol. of CC14 (on pinene) for 4-6 hours using 2 per cent. $FeCl_3$ as catalyst. The resulting ester is saponified by 50 per cent. aqueous NaOH. The crude borneol has m.p. 182–183°. Pure borneol has m.p. 203–204° ; but the melting point is readily depressed.

This crude borneol on oxidation gives only a 40 per cent. yield of camphor. Hence in spite of the same yield of borneol as that of salicylic acid method, this acid is not suitable for the conversion of pinene to borneol.

Use of trichloracetic acid.—Trichloracetic acid gives a 17 per cent. yield of crude borneol from pinene ; but this " Borneol " gives very little camphor on oxidation.

Use of Salicylic acid.—In the transformation of pinene to bornyl ester, salicylic acid gives the best result out of all the acids examined. The process finally determined by trials in which time of heating, temperature and proportion of reactants (see tables below) were varied one by one is as follows :—

Pinene and salicylic acid (1·75 mols) are heated at 100–110° for 60 hours. After the reaction is complete, unchanged acid is eliminated by neutralising with aq. sodium carbonate and the remaining mixture of ester and pinene separated, dried over $CaCl_2$ and fractionated under reduced pressure (178–182° at 7 mm.) when 31 per cent. of the original pinene is recovered. From the aq. portion 80 per cent. of the unacted acid is precipitated by a mineral acid. The recovered pinene and salicylic acid are reused with addition of fresh acid to make up the required amount, until all the pinene is converted. The final yield of ester obtained is 50·5 per cent. reckoned on the wt. of pinene used, or 25 per cent. of theory. The sequence of operation is as follows :-

Operation No.	Wt. of pinene used	Wt. of acid used	Wt. of ester obtained	Wt. of pinene recovered	Wt. of pinene consumed	Wt. of acid recovered	Wt. of acid consumed	Per cent. yield of ester on wt of pinene consumed	Per cent. yield of ester on wt. of acid consumed	Per cent. yield of borneol on pinene consumed	Per cent. yield of borneol on acid consumed
1	100	200	35	31	69	150	40	25·3	43·75	18	33
2	31	62	11·5	15	16	34	28	35·9	20·5	26·6	15·5
3	15	30	4	5	10	20	10	20	20	14·8	15
Over all yield	100	200	50·5	5	95	136	78	26·5	32·4	19	20

The yield of the ester is not increased by using condensing agents like sulphuric acid, zinc chloride, sodium acetate, etc., catalysts, solvents or diluents and compounds of the acid itself like ethyl, methyl, or propyl salicylate.

The following are the yields (w. r. t.) (with respect to theory), in one operation of borneol obtained by varying proportions of reactants, temperature and time, one at a time :—

Temp. 110°. Time 60 hours. Acid 1·75 mols. Acid 1·75 mols.
1 mol pinene.   Time 60 hours.   Temp. 110–110°

Quantity of acid used in mols	Per cent. yield borneol w.r.t. theory on pinene consumed	Temp in °C	Per cent. yield bornel w. r. t. theory on pinene consumed	Time in hours	Per cent. yield borneol w. r. t. theory on pinene consumed
0·75	10	80–90	6	10	5
1·00	12	90–100	15	15	7
1·25	14	100–110	18	20	9
1·50	15	110–120	17·5	25	11
1·75	18	120–130	17	30	12
2·00	18	130–140	16	35	14
2·25	18	140–150	16	40	15
2·50	18			45	16
				50	16 5
				55	17
				60	18
				65	18
				70	18

It will be seen from the above tables that 1·75 mol. of acid is necessary, and that the temperature and time should be 100–110° and 60 hours respectively.

As regards the hydrolysis of the salicylate, various hydrolysing agents have been tried. With alcoholic potash the saponification goes smoothly and effectively. Equally good results can be obtained with aqueous sodium hydroxide. A small increase in yield is effected by the use of solid caustic soda, which has not hitherto been suggested. Calcium hydroxide gives a poor yield of borneol (20 per cent.).

The following are the results of systematic experiments, with aqueous and solid caustic soda ; graphs are also given. [Graphs 1 and 2].

AQUEOUS CAUSTIC SODA
2·5 mols of NaOH per mol of ester

Time 9 hours			Concn. 65 per cent.	
Per cent. Concn.		Per cent. yield	Time in hours	Per cent. yield
10	.. ..	....	1	....
20	.. ..	....	2	....
30	.. ..	....	3	30
40	.. ..	44	4	35·7
50	.. ..	62	5	44
60	.. ..	68	6	53
70	. ..	68	7	62
80	.. ..	68	8	68
			9	63
			10	68

SOLID CAUSTIC SODA
[Graphs 3 and 4]

Time 9 hours			2·75 mols of alkali per mol of ester	
Quantity of base (in mols)		Percentage yield	Time in hours	Percentage yield
1·00	.. .	21	1	44
1 25	.. ..	27	2	46 2
1·50	.. .	34	3	50
1·75	.. ..	41	4	53
2·00	.. ..	46	5	57
2 25	.. ..	55	6	60
2 50	.. ..	71	7	64
2·625	.. .	73–75	8	71
2·75	.. ..	73–75	9	73–75
2·875 •	.. ..	73–75	10	73–75
3·00	.. ..|	73–75	11	73–75

PINENE HYDROCHLORIDE ESTERS ISOBORNEOL

This step has been thoroughly explored by previous workers under varying conditions using a variety of reagents. In spite of this a satisfactory yield of isoborneol has not been obtained. A large number of supplementary experiments with cataysts have been tried but the efforts to improve the yields of esters have proved unsuccessful. Experiments with solvents gave no better results. Particular attention was paid to acetic acid on account of its ready availability.

The following table shows the maximum yield of isoborneol for each acid specified :—

Experiment No.	Acid used	Percentage yield of Isoborneol	Optimum conditions	Remarks
1	Acetic Acid ..	18	Gl. acetic 4 mols. Soda-cetate : 1 mol. ZnCl₂ : 5 per cent. Refluxed at 130° for 18 hours.	
2	Formic acid ..	15	Sealed tube at 200° for 18 hours with 1 mol. sodium formate.	Gl. acetic is the best. The ester yield is 69 per cent. ; but the isoborneol yield is poor.
3	Propionic acid ..	12	ZnCl₂ 2 per cent. as condensing agent.	
4	Butyric acid ..	13	With Sodium butyrate refluxed at 140–150° for 15 hours.	
5	Stearic acid ..			
6	Palmitic acid ..	....	....	Unsuccessful. Higher fatty acids not suitable.
7	Oleic acid ..			
8	Salicylic ..	14	Time 50–55 hours.	
9	Oxalic ..	10	FeCl₃ 2 per cent.	
10	Phthalic ..	7	H₂SO₄ : 4 per cent.	
11	Tetrachloro-phthalic	12	H₂SO₄ : 4 per cent.	

In most cases the " borneols " were crude and gave poor yields of camphor on oxidation.

CAMPHENE ESTERS ISOBORNEOL

Camphene can be " esterified " easily. The acids tried with pinene were used with camphene and invariably better results were obtained,

The cheapest and the most suitable acid is acetic acid. Camphene (100 gms.) and gl. Acetic acid (250 gms.) were heated together at 45–55° C. for $2\frac{1}{2}$ hours with a catalyst such as 50 per cent. H_2SO_4 (20 gms.). After completion of the reaction, anhydrous sodium acetate (18 gms.) was added to the reddish coloured liquid to remove the sulphuric acid, which otherwise caused decomposition during the recovery of acetic acid by distillation. Acetic acid (187·5 gms.) was distilled off (oil bath) up to 130–135°C. and was used again. The residual ester (118 gms.) was washed with aq. Na_2CO_3 and with water and was used without further purification. The final yield of ester was 82 per cent. of the theoretical. It is hydrolysed by aq. or solid caustic soda to yield isoborneol. The b.p. of the various esters are given in the following table :—

Isobornyl ester	Acetate	Formate	Prepionate	Butyrate	Salicvlate	Oxalate
B.P. °C at mm. ..	100_{14}	107_{13}	150_{13}	123_{11}	$171-173_5$	$157-160_{680}$

With oxalic and salicylic acids the yields are not so good. Various other acids have been tried and the best yields of isoborneol obtained under various conditions and with different reagents are tabulated :—

Experiment No.	Acid used	Percentage yield of isoborneol	Optimum conditions	Remarks
1	Acetic acid ..	64	50 per cent. H_2SO_4; 0·12 part. Temp. 70–80° for 4–6 hours. $ZnCl_2$; 2 per cent.	Acetic acid is the best.
2	Formic Acid ..	35		
3	Propionic Acid ..	37		
4	Butyric Acid ..	36		
5	Stearic Acid ..			
6	Oleic Acid ..	....	....	Unsuccessful higher fatty acids not suitable.
7	Palmitic Acid ..			
8	Salicylic Acid ..	29·5	Time 30 hours.	
9	Oxalic Acid ..	18	Time 4–6 hours at 99–100°.	
10	Phthalic Acid ..	12	$ZnCl_2$: 2 per cent.	
11	Tetrachlorophthalic Acid	10	H_2SO_4 : 4 per cent.	

The maximum yield of isoborneol from isobornyl acetate was 80 per cent.

The following table gives the best percentage yields of the esters and borneols from pinene, pinene hydrochloride and camphene :—

Substance	Method	Ester yield	Borneols yield
Pinene	Salicylate	25	18
Pinene Hydrochloride	Acetate	69	15
Camphene	Acetate	82	67

It is not out of place in this connection to mention a few words about the yield of isobornyl ester from pinene hydrochloride and the resulting poor yield of isoborneol. A yield of 82 per cent. of ester is claimed by Dubosc and Luttringer (Bull. Soc. Ind. Rouen, *48*, 83), which on repetition by us gave a maximum yield of 63 per cent. Further this ester gave on hydrolysis only a maximum yield of 15 per cent. of isoborneol. Hence the ester obtained must be impure.

Hence pinene and pinene hydrochloride are not suitable for the direct production of borneols and thence camphor. Camphene appears to be a necessary step in the process.

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        State Laboratory, Dublin.   [*Received July 29, 1941*]

FIGURE.1.

HYDROLYSIS OF BORNYL SALICYLATE

(AQUEOUS NaOH)

TIME 9 HOURS

1gm. MOL OF ESTER
2·5GM. MOL OF Na OH USED
IN VARYING CONC N.

CONCENTRATION OF NaOH

FIGURE 2.

Conc n of NaOH = 65%

2·5GM. MOLS OF Na OH PER GRAM
MOL OF ESTER

FIGURE 3 |

HYDROLYSIS OF BORNYL SALICYLATE

(SOLID NaOH USED)

TIME 10 HOURS

CAUSTIC SODA IN GRAM MOLS

FIGURE 4.

2·75g. MOLS PER GRAM MOL OF ESTER

(SOLID NaOH USED)
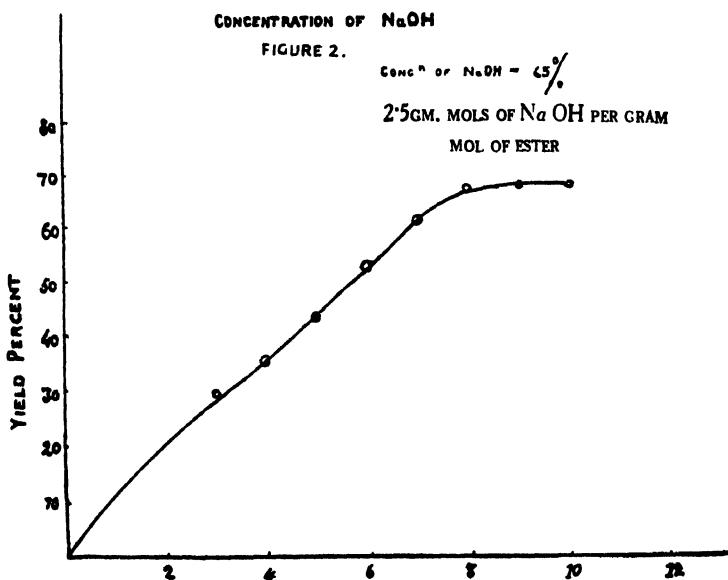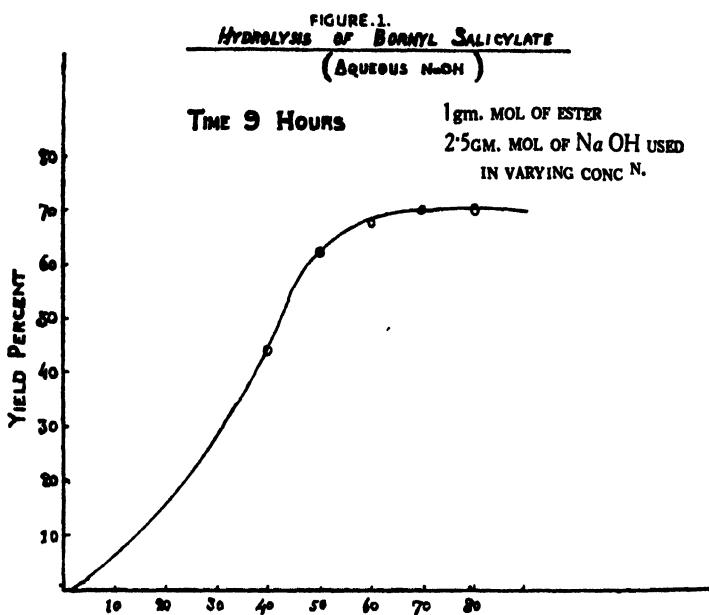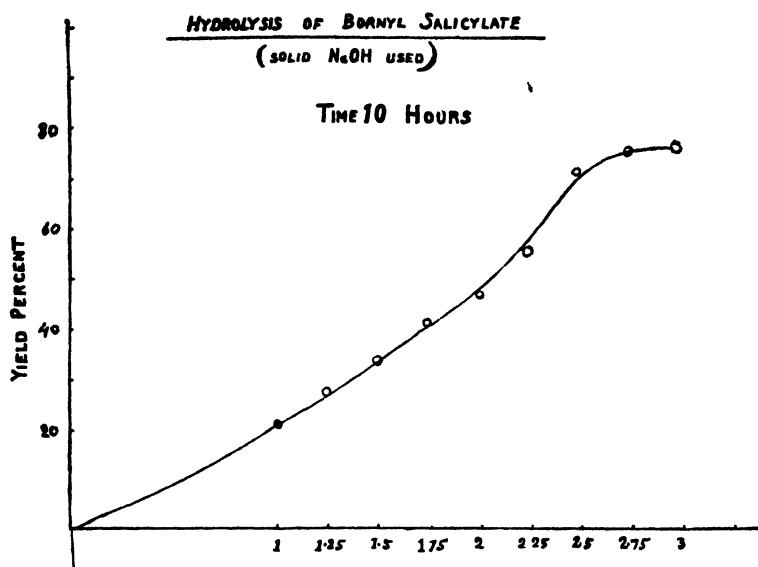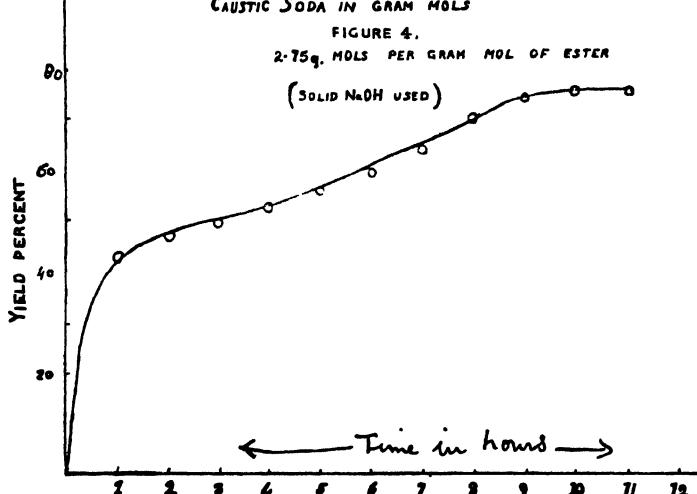
CHROMONES OF THE NAPHTHALENE SERIES—
Transformation of O-Aroyloxyaceto Arones into O-Hydroxy-Di-Naphthoyl Methanes

By

V. V. ULLAL, R. C. SHAH AND T. S. WHEELER

IN continuation of our previous work of the transformation of o-aroyloxyacetoarones into o-hydroxy-di-naphthoyl methanes by the action of sodium ethoxide (Ullal, Shah and Wheeler, J.C.S., 1940, 1499) and thereby the preparation of the chromones by cyclisation with hydrobromic acid, nitropaeonol was condensed with various acid chlorides and subjected to transformation reaction under various conditions when the original hydroxy ketone and the respective acids separated. Evidently it is apparent that sodium ethoxide was acting as a hydrolysing agent rather than a transformation agent. Ordinarily, when the migration of the acyl-group is taking place, hydrolysis takes place to a certain extent, which, consequently results in the yield being varied, although quantitative yield is expected. This discrepancy in the yield in different cases may, moreover, be due to change in the degree of hydrolysis as a result of change of condition, and the consentration of sodium ethoxide solution and the nature of the acyl group. In the present cases, the presence of a negative radical such as—NO_2 group, appears to have completely inhibited the migration of the acyl group, thereby accelerating the action of hydrolysis to such a preponderating extent that the products of hydrolysis are only separated.

In the synthesis of 2-styryl chromones, when Cinnamoyl—2-hydroxy-1-naphthoyl methane was treated with sodium ethoxide solution, gave 2-styryl-5 : 6-benzochromone, instead of the corresponding hydroxy ketone. Sodium ethoxide simultaneously acted both as the transforming and dehydrating reagent. There are instances where transformation reagents, such as sodium in toluene, behaved as dehydrating reagent (Virkar, Wheeler, J.C.S., 1939, 1679).

EXPERIMENTAL

2-Benzoyloxy-4-methoxy-5-nitroacetophenone was obtained, from nitropaeonol (15g.), benzoyl chloride (10g.) and pyridine (20 c.c.), and separated from alcohol in colourless short thick needles (12g.) with m.pt. 133°C. (Found, N-4·93 per cent.; $C_{16}H_{13}O_6N$ requires N-4·62 per cent.)

2-Benzoyloxy-4-methoxy-5-nitroacetophenone (2g.) was treated with sodium ethoxide solution (0·1g. sodium) and had been kept at room temperature for few minutes. On acidification with dilute acetic acid the original nitropaeonol and benzoic acid separated.

2-(1'-Naphthoyloxy)-4-methoxy-5-nitroacetophenone was similarly obtained from nitropaeonol (10g.), α-naphthoyl chloride (10g.) and pyridine (20 c.c.) and separated from alcohol in brown fine needles m.pt. 146-'48°C. (Found, N-4·13 per cent. $C_{20}H_{15}O_6N$ requires N-3·84 per cent.)

The above on treating with sodium ethoxide gave the original nitroketone and α-naphthoic acid.

2-Cinnamoyloxy-1-acetonaphthone (4·5g.) was obtained from 2-hydroxy-1-acetonaphthone (5g.), Cinnamoyl chloride (4g.) and pyridine (15 c.c.), and separated from alcohol in fine long colourless needles with m.pt. 127-'28°C. (Found, C-77·2 per cent., H-4·8 per cent., $C_{21}H_{13}O_6$, requires C-77·3 per cent., H-4·9 per cent.)

2-Styryl-5 : 6-benzochromone. 2-Cinnamoyloxy-1-acetonaphthone (2g.) was treated with sodium ethoxide solution (0·2g. sodium) and had been kept at room temperature for few minutes. On acidification with dilute acetic acid and on further dilution the product separated which on crystallisation with alcohol gave fine wooly needles m.pt. 197-'98°C. (Dey and Lakshminarayan J. I. C. S., 1932, 154, gave the same melting point). It exhibited green fluorscence with concentrated sulphuric acid.

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A NOTE ON THE CONDENSATION OF CHLORAL WITH ETHYL ACETOACETATE

By

D. R. KULKARNI AND N. M. SHAH

IN connection with another investigation on the effect of α — substituents in the acetoacetic ester molecule in the Pechmann condensation (Kulkarni, Alimchandani and Shah N. M., J. Indian C. S. 1941, *18*, 113), ethyl α —(α —hydroxy-β β β-trichloro-ethyl)-acetoacetate was required in large quantity. The condensation of chloral with ethyl acetoacetate was thought of as a convenient method for its synthetical preparation. Claisen and Mathews (Annalen, *218*, 175) condensed chloral with acetoacetic ester in presence of acetic anhydride by heating the components in a sealed tube. The product boiling at 154–158°/24–26 mms. was assigned the constitution, ethyl β-trichloro-methyl—α-acetyl-acrylate :

$$CH_3CO.\ CH_2.\ COOEt + CCl_3CHO = CH_3CO.\ C.\ COOEt + H_2O$$
$$CH.\ CCl_3$$

Shaikh (M.Sc. Thesis, Bom. Univ., 1931) tried the same condensation in presence of pyridine and isolated a product, b.p. 135°/22–25 mms., to which he assigned the structure, $CH_3CO.\ CH\ (CH.OH.CCl_3).$ COOEt. The exact conditions described by Shaikh were carefully followed ; it was, however, found that the oil, even on distilling under lower pressures did not give the product as claimed by Shaikh. It may be mentioned that the smell of chloral vapours was distinct in the fractions collected during the distillation. The purified product that was obtained according to Shaikh on condensation with resorcinol in presence of sulphuric acid gave 7-hydroxy-4-methyl-coumarin, thus indicating that the product was unchanged ethyl acetoacetate. Repetitions of Shaikh's method to obtain α-(α-hydroxy-β β β-trichloro-ethyl) substituted product led to repeated failures.

After several trials, the required ethyl α-(α-hydroxy-β β β-trichloro-ethyl)-acetoacetate could be obtained and the conditions for its preparation standardised. The mixture of acetoacetic ester (1 mol.) and freshly distilled chloral (1·2 mols) in presence of pyridine (1 c.c. for 11 gm. of the ester-chloral mixture) was kept at room temperature (25–30°) for 5 days. On working up the reaction-mixture (*vide* experimental), a heavy oil was obtained. Various attempts to distil it even under very low pressures led to its decomposition. It is unstable to heat. It is clear that Shaikh's claim to have obtained α-(α-hydroxy-β β β-trichloro-ethyl)-acetoacetic ester by the procedure he followed cannot be substantiated.

The structure assigned by us to the product obtained rests on the following grounds : (*i*) it gives a positive test for chlorine, (*ii*) on Pechmann condensation with resorcinol, it gives 7-hydroxy-3-(α-hydroxy-β β β-trichloro-ethyl)-4-methylcoumarin (Kulkarni, Alimchandani and Shah N. M., loc. cit.).

It is well known that pyridine brings about the O-C linkage in acetoacetic ester. It is interesting to note that in the above condensation C-C linkage is effected, possibly due to the large inductive effect of -CCl$_3$ group.

<center>EXPERIMENTAL</center>

The procedure given below has been found to give a good yield of the α-(α-hydroxy-β β β-trichloro-ethyl)-acetoacetate.

Pyridine (21 c.c.) was gradually added to a mixture of ethyl acetoacetate (100 g.) and chloral (135 g.) with cooling and shaking. The addition of pyridine causes the rise of temperature which is prevented by adding a small quantity at a time and cooling till the mixture attains ordinary temperature. After keeping the mixture for a period of 5 days at room temperature (change in the period considerably affects the yield) it was poured into water when an yellow oil separated. It was thoroughly washed with water followed by cold dil. sulphuric acid, in order to remove excess of chloral and pyridine respectively. It was then extracted with ether and the ethereal extract washed well with water till it was not acidic to litmus. The ethereal layer was then dried over calcium chloride and ether removed, when a heavy oil was obtained. It was kept in a desiccator over paraffin to remove the last traces of ether ; yield, 155 gms. Attempts to distil even at a low pressure yielded unchanged acetoacetic ester, chloral vapours being evolved. The undistilled product was analysed. (Found : Cl, 37·58. C$_8$H$_{11}$O$_4$Cl$_3$ requires Cl, 38·4 per cent.). D$_4^{30}$= 1·328. Ethyl α-(α-hydroxy-β β β-trichloro-ethyl)-acetoacetate gives cherry red colouration with alcoholic ferric chloride solution. The undistilled product has been satisfactorily used in all work. This is analogous to the use of acetone dicarboxylic acid without being isolated.

The *acetoxy* derivative was prepared by adding a few drops of conc. H$_2$SO$_4$ to the mixture of the ester and acetic anhydride and keeping the mixture overnight : colourless liquid, b.p.120°/7 mms. (Found : Cl, 32·85. C$_{10}$H$_{13}$O$_5$Cl$_3$ requires Cl, 33·3 per cent.).

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A NOTE ON THE CONDENSATION OF MALEIC ANHYDRIDE WITH NAPHTHOL METHYL ETHERS

By

K. P. Dave, K. V. Bokil and K. S. Nargund

THE condensation of maleic anhydride with phenol ethers by Friedel and Craft's reaction has been described by various workers. (Pechmann, Ber, 1882, *15*, 881. Gabriel and Coleman, Ber, 1899, *32*, 397. Rice, J. A. C. S. 1923, *45*, 228. *ibid*, 1924, *46*, 218. *ibid*, 1931, *53*, 3153. Dave and Nargund, Jour. Bom. Univ. 1938, VII, part 3, page 191). It has been shown that an unsaturated keto acid is the only product in all cases except in case of resorcinol dimethyl ether where, in addition to the unsaturated acid, a substituted succinic anhydride and a disubstituted keto acid are also obtained. The present communication deals with the condensation of maleic anhydride with naphthol methyl ethers.

Condensation of maleic anhydride with α-naphthol methyl ether using nitrobenzene as solvent gave, 88 per cent. yield of β-4-methoxy-1-naphthoyl acrylic acid. The constitution of this acid was proved by oxidation when 4-methoxy-1-naphthoic acid was obtained. Methyl and ethyl esters of this acid were gummy masses which solidified to reddish resins but could not be purified by crystallisation. α-β-Dibromo-β-4-methoxy-1-naphthoylpropionic acid obtained by addition of bromine to the above acid had m.p.160°, the constitution of which was proved by analysis and oxidation.

Condensation of β-naphthol methyl ether under the same conditions gave a product m.p.105-120° which could not be purified by any means. That it contained mainly β-2-methoxy-1-naphthoyl-acrylic acid was shown by oxidation when 2-methoxy-1-naphthoic acid was obtained in quantity.

EXPERIMENTAL

The yields of the condensation products obtained by following the procedure of Dave, Bokil and Nargund (loc. cit.) are given below :—

Methyl ether used		Product obtained	Yield
α-Naphthol ether	methyl	β-4-methoxy-1-naph-thoyl-acrylic acid	88 per cent. in nitro-benzene
β-Naphthol ether.	methyl	β-2-methoxy-1-naph-thoyl-acrylic acid Impure	80 per cent, in nitro-benzene

β-4-methoxy-1-naphthoyl-acrylic acid.—In order to get this acid in pure condition it was necessary to wash the crude condensation product with hot water several times. It was soluble in ethyl acetate and acetic acid and insoluble in benzene, chloroform, petrol, and water. It was sparingly soluble in hot alcohol from which it separated in green rectangular plates. It was best crystallised from ethyl acetate-petrol mixture m.p. 192–193°. (Found : C, 70·1 ; H, 4·8 per cent. Eq. wt. 254. $C_{15}H_{12}O_4$ requires C, 70·3 ; H, 4·7 per cent. Eq. wt. 256).

Oxidation of β-4-methoxy-1-naphthoyl-acrylic acid.—The acid (2 gms.) dissolved in a small quantity of sodium hydroxide solution was treated in cold with a solution of potassium permanganate (6·5 gms.) in water (400 c.c.). It was then worked in the usual manner. The product obtained had m. p. 230° and did not depress the m. p. of 4-methoxy-1-naphthoic acid. Rousset, (Bl, 3, *17*, 308).

α-β-Dibromo-β-4-methoxy-1-naphthoyl-propionic acid.—It was obtained by adding theoretical quantity of bromine dissolved in acetic acid to the above acid also dissolved in acetic acid. It crystallised in granules from dilute acetic acid, m. p. 160°. (Found : Br, 38·6 per cent. Eq. wt. 412. $C_{15}H_{12}O_4Br_2$ requires Br, 38·5 per cent. Eq. wt. 416). On oxidation it gave 4-methoxy-1-naphthoic acid.

β-2-methoxy-1-naphthoyl-acrylic acid.—It could not be obtained in pure form for analysis. It had m.p. 105–120°. On oxidation with alkaline potassium permanganate it gave 2-methoxy-1-naphthoic acid m.p. 176 .

We thank the Charak Trust for the gift of chemicals.

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ACOUSTIC PROPERTIES OF THE GOL GUMBAZ, BIJAPUR

By

G. R. PARANJPE

THE Gol Gumbaz at Bijapur is one of the few large buildings in the world with notable proportions and a magnificent dome. It is now merely an ancient Indian monument, having been built in the year 1656 A.D. as the tomb of Sultan Muhammud Adil Shah. Gol Gumbaz is a remarkably simple building for all its size, just a great square hall enclosed by four lofty walls, but tressed up by octagonal towers at the corners and the whole surmounted by an enormous and spherical dome. The extreme outside measurement of the Mausoleum, including the dome, is 205 square feet. The extreme height to the apex of the dome from the base of the building is 198 feet 6 inches, the exterior diameter of the dome is 144 feet, while the interior diameter measures 124 feet 5 inches and the great hall, below, with no intermediate support of any kind inside its walls, is 135 feet 5 inches square. The interior height from the level of the floor, around the tomb platform, to the top of the dome is 178 feet. Within the base of the dome is a broad gallery, 11 feet wide, which hangs out into the interior of the building, 109 feet 6 inches above the floor. The total area covered by the dome of Gol Gumbaz is 18,109 square feet. It is the largest space covered by a single dome in the whole world. The next largest dome being that of the Pantheon at Rome. The diameter of the Pantheon dome is 142 feet and the area covered below is only 15,833 square feet.

As a piece of architecture, there is really nothing to match this structure of Gol Gumbaz. The system of pendendtives is, without doubt, the most successful and the most graceful method of construction of such domes. This system is famous in India. The architect, who conceived and carried out to such a successful issue the very stupendous task of hanging a mighty dome right across the whole expanse of the outer walls, has indeed executed a remarkable feat. But it is most unfortunate that the architect should have passed into oblivion, his very name is now unknown.

The Gol Gumbaz at Bijapur possesses remarkable acoustic properties. They are mainly :—

(i) the Whispering Gallery effect,
(ii) the Multiple Echo effect,
and (iii) the very large reverberation time.

As to these effects as found in the Gol Gumbaz, they are generally described in books and passed down from generation to generation, but there is absolutely no authentic or quantitative record ever made, so that it is difficult to say whether the effects observable today are as good or better or worse than they were some years ago.
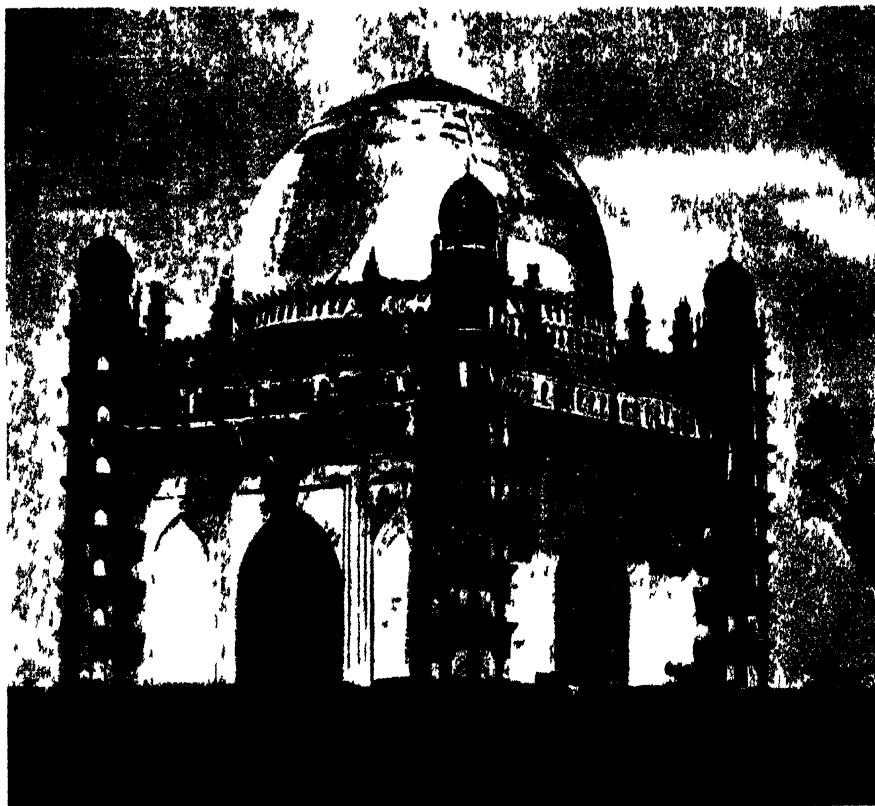
Gol Gumbaz Bijapur

Taken from Picturesque India (p 31) by Mr M Hucrhmrr, Bombay, 1928.

References to the architectural features and the remarkable acoustic effects, are made in the books written by J. Fergusson[1] and H. Cousens[2, 3]

The following is an extract from Cousens[3].

" A remarkable feature of the building is its Whispering Gallery....... The sounds that assail one on entering the chamber below, are much intensified upon stepping into the gallery by a passage through the dome, when the footfall of a single person is enough to awaken the echoes of the tread of a company. Strange wierd sounds and mocking whispers emanate from the walls around. Loud laughter is answered by a score of fiends hidden behind the plaster. The slightest whisper is heard across from one side to the other, the ticking of a watch being distinctly audible while a single loud clap is echoed even ten times distinctly...... "

Most of the acoustic phenomena are noted in Fergusson's [1] book where echo is clearly explained although there the term *resonance* is loosely applied to indicate confused sound or reverberation. The author says: " It requires rather more than 65 feet between a person and the reflecting surface in order that the sound of his voice may, on return, reach his ear after the cessation of the original sound and so create the impression of a second sound or echo. If greater distance intervenes, the echo is more distinct.......... If the distance is less, no distinct echo results, as the original and reflecting sounds overlap and produce a confused sound or resonance." The description of the multiple echo appears to be, however, realistic. The author[1] says : " ...... the sound is bandied backwards and forwards, producing a series of echoes, each time losing some of its intensity until it becomes too feeble to catch the ear........ "

An attempt was made to collect any previously obtained data regarding the whisper and the persistence of multiple echoes. But, unluckily, not much information was available, and whatever little could be collected was found to be very unreliable. Some people asserted that the acoustic effects are nowadays not so good as they were some years ago. Some said they could hear a watch very distinctly across the diameter of the gallery. Even this could not be verified because modern watches make practically no audible sound. The archaeological supervisor who is in charge of the place over 15 years is perhaps the only observer who definitely said that there was no change in the acoustic phenomena.

(*i*) THE WHISPERING GALLERY EFFECT

According to W. C. Sabine[4] the term Whispering Gallery usually indicates a room either artificial or natural so shaped that faint sounds can be heard across extraordinary distances.

[1] James Fergusson, History of Indian and Eastern Architecture, Vol. II, p. 273. John Murray, London, 1910.

[2] Henry Cousens, Archaelogical Survey of India, Vol. XXXVII, Imperial Series, p. 98. Govt. of Bombay, 1916.

[3] Henry Cousens, The Architectural Antiquities of Western India, p. 71. India Society, London, 1926.

[4] W. C. Sabine, Collected Papers on Acoustics, 1927, pp. 255–276.

The Gol Gumbaz at Bijapur is noted in India for its Whispering Gallery effect, although it is, unfortunately, not mentioned along with the six most famous galleries, among which the Dome of St. Paul's Cathedral, London, and the Statuary Hall in the Capitol Washington are referred to very often.

A gallery becomes a whispering gallery on account of either of the two reasons. It has either (*i*) the sound travelling along the circular reflecting surface or it has (*ii*) the sound coming to a sharp focus owing to reflection on the curved surface of a spherical or an ellipsoidal dome.

The whispering effect in the St. Paul's Cathedral, London, has been very carefully investigated. It is of the first type mentioned above. A. E. Bate[5] has given a complete account of such phenomena and he has quoted all references in this connection.

The whispering gallery in the Gol Gumbaz, Bijapur, is also of the second type, i.e., it possesses whispering and multiple echo effects. It is situated within the base of the dome. It is 11 feet wide and its outer diameter is 124 feet, 5 inches. The gallery hangs out into the interior of the building 109 feet and 6 inches above the floor. The back of the gallery appears to be almost a vertical cylindrical surface about 10 or 15 feet high, and the dome is supposed to be a hemispherical bowl about 62 feet in radius. (Accurate shape of this dome and the height of the circular wall are not available).

Scale of [_____] feet
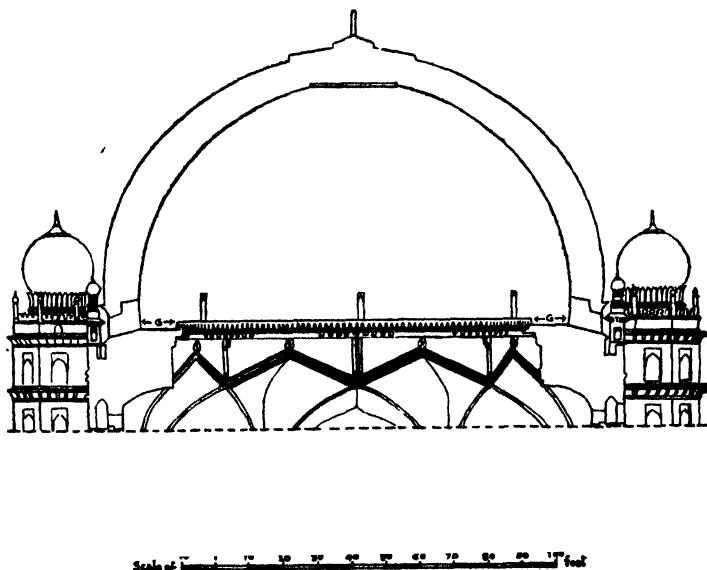
Cross Section of the Dome and Gallery in the Gol Gumbaz, Bijapur

[5] A. E. Bate, Proc. Phys. Soc. London, *50*, 1938, p. 293.

In the Gol Gumbaz benches are provided at four places at equal distances in the gallery and they are very close to the wall. When a man, sitting on one bench, whispers near the wall, he can be heard at any point of the circumference. But the effect is best pronounced when the speaker and the hearer are at the opposite ends of a diameter. Under ordinary conditions a whisper is hardly audible at a distance of five or six feet. It is, therefore, impossible that a whispering sound in the gallery can be carried acorss, along the diameter which is about 124 feet. Rayleigh gave the explanation that the sound comprising of the whisper creeps round the gallery horizontally and along the wall. The effect becomes more pronounced in a whisper because the sound traversing directly across the diameter is imperceptible. The sound which is heard really travels round the wall by successive reflections along short chords. This sound suffers very little absorption at the hard smooth wall during reflection.

C. V. Raman[6] and Sutherland confirmed these conclusions by carrying out investigations in the St. Paul's Cathedral, London. Raman[7] examined and reported on many Indian Whispering Galleries and he only mentioned the Gol Gumbaz as a notable gallery.

The experiments of Raman were repeated recently in the Gol Gumbaz and it was found that the sound waves do actually run round the walls as Rayleigh and Raman suggested. When the circular wall is tapped at one point the sound waves produced by this tap travel in opposite directions along the wall; one wave goes clockwise and the other anticlockwise. They meet together at the opposite end of the diameter and, being exactly in phase, reinforce each other, with the result that the sound becomes distinctly audible. The waves, however, continue to run and meet again at the source to produce the *first echo*. Since this journey causes only very little loss of energy the waves proceed and bring about second, third, fourth or more echoes. It is possible to measure the time period between a given number of six or ten distinctly audible echoes and calculate the velocity of the sound. This comes out in fair agreement with the velocity of sound in open air.

An investigation was made in the whispering gallery to verify the theoretical results that the higher frequency notes that travel closer to the wall than the lower frequent notes. Experiments were done using an audio-frequency signal generator whose volume could be controlled and measured. The results confirmed the theoretical expectation that when the sound is produced at one end of the diameter and received at the other, *the audibility improves with the higher frequency notes*. The whisper differs from ordinary speech inasmuch as the former contains more of high frequency notes. It is, therefore, apparent that the circular walled gallery very naturally becomes a good whispering gallery. The

[6] C. V. Raman and Sutherland, Proc. Roy. Soc. *100A*, 1921–22, p. 424.
[7] C. V. Raman, Proc. Ind. Association, Cult. Sci. 8, 1921–22, p. 159.

loss of sound energy is less in a whisper made close to the wall than in a loud speech. The loud speech produces echoes to be distinctly audible but that effect is entirely different from the whispering gallery effect.

It is now established[8] that the necessary conditions for the whispering gallery effect are,

(*i*) a hard circular vertical wall for good reflections,

(*ii*) a source of sound of sufficiently low intensity to suffer no appreciable reflection from the opposite side of the gallery and

(*iii*) a source near the wall and directed so that the angle of incidence is large.

All the conditions are remarkably fulfilled in the whispering gallery of Gol Gumbaz at Bijapur.

(*i*) The circular wall is smooth, hard, and vertical and appears to be over 15 feet in height. The dome does not appear to take any part in the whisper except perhaps when it is entirely hemispherical with no straight portion of the wall. The sound can then travel either along the gallery or along the perfectly hemispherical dome, in the latter case, merely to be reflected normally on the floor of the gallery without loss of any kind. Even if the wall had a small flat vertical height these conditions would not be materially altered.

(*ii*) The distance of 124 feet across the gallery is well beyond the audibility limit of ordinary low voices, so as to exclude possible direct reflection from the opposite wall.

(*iii*) The circle being very large, with 62 feet radius, the angle of incidence is nearly 90 degrees.

In popular language one speaks of a whisper as a feeble sound. Actual experimental observations, carried out, ascertained that really very small and measureable amounts of sound energy can be audible in the Gol Gumbaz. Experiments were made on pure notes ranging from 700 cycles per second to 3000 cycles per second and they were distinctly heard at the opposite end of the whispering gallery when their energy outputs were gradually reduced to $0\cdot4$ microwatts and $0\cdot025$ miscrowatts respectively. The time of the investigation was morning and there was not that absolute silence as one would wish to have for such work. Sparrows were sending their own notes and if it were possible to have perfect silence still smaller sound outputs would have been audible.

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[8] Ghosh and Rai, A Text-Book of Sound, 1940, p. 264.

Below are given from standard works [9, 10, 11] some numerical illustrations to indicate what magnitudes of sound energies are involved in ordinary sounds, conversations and whispers.

Types of sound emitter	Output of sound energy
15 million loud speakers ..	.. 1 Horsepower.
1 average loud speaker ..	.. 50 microwatts/cm.^{2}
Speech in average conversation	.. 10 microwatts/cm.^{2} or 100 ergs. per sec.
Loudest possible speech ..	.. 1000 microwatts/cm.^{2}
Weak voice (not whisper)	.. 0·1 microwatts/cm.^{2}
Very soft whisper ..	.. 0·001 microwatts/cm.^{2}

(ii) THE MULTIPLE ECHO EFFECT

When a gallery is not of the whispering type, caused by its circular wall, it is usually of the focussed echo type. In such a case the original sound travels across space in different directions, over sufficiently long distances and gets reflected to cause the sound energy to be focussed once or twice or thrice depending on the intensity of the sound and the perfectness of the reflecting surface.

Sabine[4] mentions in this connection that in galleries of this type the surfaces are not theoretically correct and therefore the phenomena of whispering effect or distinct echo are far from perfect. This failure of loudness and distinctness in most of the known multiple reflection galleries arises not from any progressive loss in the many reflections, for the loss of energy in reflection is practically negligible. There are few galleries of this type. St. John Lateran in Rome is one such. It is obvious that most accurate fulfilling of the surface-focussing conditions cannot be accidental.

Gol Gumbaz at Bijapur is remarkable in this respect also. It has the circular wall of the gallery causing the most beautiful whispering effect, it has sufficiently large proportions with a perfect dome which renders multiple echoing not only possible but most successful. The circular gallery produces multiple echoes most conveniently because the sound actually travels round the wall in opposite directions, and does so any number of times with practically no loss of energy. In addition to these there are reflections from the wall portions, exactly opposite the source, with the result that the sound is bandied backwards and forwards, producing a series of echoes, each time losing some of intensity until it becomes too feeble to be audible. Books have mentioned that the number of echoes vary between 7 and 9.

[9] H. Davis, An introduction to the study of Noise Problems, p. 29, 1936-37.
[10] Glover, Practical acoustics for the constructor, p. 106, 1933.
[11] Ghosh and Rai; A Text-Book of Sound, 1940, p. 119,

In reality when very careful counting was made by the author on sharp impulsive sounds (of extremely small duration) the echoes appeared to be lying between 22 and 25. The experiments carried out at the Gol Gumbaz have enabled a regular gramophone record to be made wherein the number of the echoes can be actually counted.

The results which visitors notice like single footsteps appearing to be the tread of a company of people or the sound of thunder when only a tough paper is torn quickly are really effects of multiple echoes.

It is necessary that the true natures of the circular wall and the surface of the dome should be maintained, àt its existing quality. If this were not done the quality of the multiple echo effect, as well as the whispering gallery effect would eventually suffer loss.

Sabine[4] has quoted, in his collected papers, on acoustics the famous case of the ceiling of the Hall of Statues in the Capital at Washington.

" The ceiling with the exception of a small circular skylight, is a portion of an exact sphere with its centre very nearly at head level.......... The ceiling is coffered..........As originally constructed, and as it remained until 1901, the ceiling was perfectly smooth, being of wood, papered and painted in a manner to represent coffering.

" In 1901 a fire in the chamber of the Supreme Court, also in the Capitol, led to a general overhauling of the building, and among other dangerous constructions the ceiling of wood in the Hall of Statues was replaced by a fireproof construction of steel and plaster. Instead of being merely painted, the new ceiling had recessed panels with mouldings and ribs in relief. In consequence of this construction the whispering gallery lost a large part of its unique quality...... "

The same case is referred to in the Sturgi's Dictionary of Architecture in an article on whispering galleries. This article was apparently written a year or two prior to the fire at the Capital, 1901. It states : " the ceiling painted, so that it appears deeply panelled, is smooth. Had the ceiling been panelled the reflection would have been irregular and the effect very much reduced."

After the fire the new ceiling was made to conform within a fraction of an inch to the dimensions of the original ceiling. Yet the whispering effect was in large measure lost.

The adverse effect of the actually recessed panelling is to prevent reinforcement of all wavelets which is a very essential condition for the whispering and multiple echo effect.

The Gol Gumbaz at Bijapur has already suffered much through ravages of weather and time. There are numerous cracks in the dome and big portions, of plaster have fallen off from the interior surface of the dome and the wall. The internal surfaces are the most essential factors in the remarkable acoustical properties of the dome.

Reflection depends on smoothness, and yet smoothness is only a comparative term when used in optics and in acoustics. In order to produce any injurious effects in reflection, a scratch, a crack or an irregularity on a smooth surface must be of the same dimensions as the incident wavelength.

Audible sound waves are $\frac{1}{2}$ inch to 60 feet long. Visible light waves are 1/40000th to 1/80000th inch long. So that it can be seen, that although a crack or a roughness (owing to fallen plaster) would cause distortion of the waves and generally reduce the efficiency of the whispering gallery, it would by no means wholly destroy the same; unless in the extreme case the reflecting surface has become completely irregular and broken up.

(iii) Large Reverberation Time

This is a property which is not characteristic of the Gol Gumbaz only. It is found in every large enclosure and it is usually described by saying that the sound, once produced lingers on for some time before it dies out; thus making intelligibility of human speech very difficult. The cause is *reverberation*[12].

Suppose a " pulse " to be produced at some point in a room. A wave of compression spreads out in all directions. In the absence of any reflecting surfaces (bodies) an auditor would receive a single sharp impression, but the walls of the room reflect the greater portion of the sound, so that a series of waves, generally diminishing in amptitude, and formed by subsequent reflections, pass the observer's ears, until all the energy of the original wave has been dissipated by friction. In place of the single compression, the observer hears a roll of sound, and the time taken for this to die away, i.e., fall below the threshold of audibility is known as the " time of reverberation " of the sound in this particular room, reckoned from the time that the original pulse was produced or, in the case of a continuous note, the time that the source stopped sounding.

When a succession of different vowels or notes are sounded the effect is that the sound is found to be pulsating and hanging on for an appreciable time. It is, however, important for distinct rendering of music or speech that each separate sound should give rise to a sufficient intensity in every part of the enclosure and then rapidly decay to give place to the next sound. This is particularly necessary with speech; for a musical note more reverberation is possible.

The interior of the Gol Gumbaz divides itself into two distinct parts (i) one part is the lower almost cubical enclosure, about 135 feet long and broad and 109 feet high up to the gallery with an open top. The volume of this is almost 2 million cubic feet; (ii) the second part is the circular gallery of diameter 125 feet and 11 feet wide with a hemispherical

[12] E. G. Richardson, Sound, 1940, p. 296.

dome of about 62 feet radius resting over a vertical cylindrical wall about 15 feet high. The volume of the cylinder together with the volume of the dome is about 0·67 million cubic feet.

The reverberation time in the Gol Gumbaz was very large and in most measurements it was observed to be about 20 seconds. A limiting reverberation of 1·03 seconds seems best for all rooms having a volume less than 10,000 cubic feet. For large and closed monuments there is usually a large reverberation. The reverberation is the only thing that occurs in the lower part of the Gol Gumbaz and it is, therefore, very difficult for people to stand at some distance from each other and carry on intelligent conversation. On the gallery, however, the effect is entirely different. Whispering is possible, owing to the circular gallery and thus the reverberation is not found to be inconvenient except when one attempts to talk loudly.

When the reverberation time is practically the same for all frequencies the effect is of a type not undesirable, but we find often that the time changes with frequency and then the effect is confusion. Under certain conditions[18] it is possible to realize that " one person singing in a chamber sounds like a full choir."

Most sincere thanks are due to the Department of Archæology, Government of Ind a, for the necessary permission and material assistance rendered to the author in conducting certain experimental measurements inside the Gol Gumbaz.

Royal Institute of Science, Bombay.

18 E. Meyer, Electro-Acoustics, 1939, p. 103.

ABSTRACTS OF M.Sc. THESES

I—Studies in Coumarins. By C. V. Deliwala, M. R. Science Institute, Gujarat College, Ahmedabad.

Part 1—*The condensation of 4-acyl-resorcinols with ethyl acetoacetate in presence of anhydrous aluminium chloride.*

Sethna, Shah and Shah (J. 1938, 228) could successfully condense resacetophenone with ethyl acetoacetate with aluminium chloride as condensing agent. Shah and Shah (J. 1938, 1424) extended this reaction to other phenolic ketones and got 5-hydroxy-coumarin derivatives, which are otherwise difficult to prepare. Thus for example, from resacetophenone, the above authors could get easily 5-hydroxy-6-acetyl-4-methylcoumarin.

As these 5-hydroxy-6-acyl-coumarins are useful materials for synthesising hetero-cyclic compounds like coumarino-chromones-flavones and other natural products containing such ring-systems, this reaction has been extended to the condensation of other 4-acyl-resorcinols. Thus the condensation of respropiophenone, resbutyrophenone, 2 : 4-dihydroxy-phenyl-benzyl-ketone and 4-p-tolouyl-resorcinol has been studied in this part.

All these ketones do not condense with ethyl acetoacetate in presence of sulphuric acid, as in case of resacetophenone. With aluminium chloride as condensing agent, the same condensation could be easily affected at 120–130° in dry nitrobenzene solution. In all cases, the condensation product obtained has been proved to be 5-hydroxy-6-acyl-coumarin derivative, the condensation taking place in ' 2 ' position of the resorcinol molecule with subsequent ring-closure.
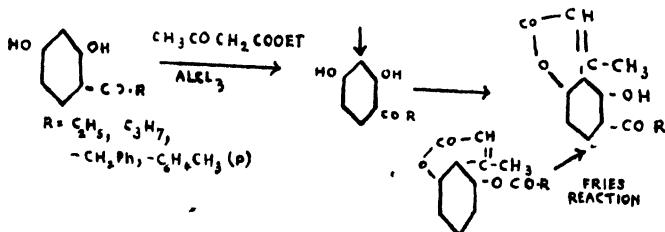
The constitution of the product obtained by the condensation of respropiophenone (R=Et) with ethyl acetoacetate has been established as 5-hydroxy-6-propionyl-4-methylcoumarin by its synthesis by the Fries transformation of 5-propionoxy-4-methylcoumarin, and (2) by the

formation of coumarino-chromone, 2′ : 3′ : 4-trimethyl-chromono-7-′ : 8′ : 6 : 5-4-pyrone, (I) m.p. 241-242′, by Kostanecki acetylation. The clemmensen reduction gave the corresponding 6-propyl-coumarin derivative.

Similarly, the constitution of the condensation products from resbutyrophenone and other ketones has been also established. The synthetical preparation of compounds like coumarino-chromones and di-coumarins has been described in the course of this work.

The mechanism of the formation of 5-hydroxy-coumarins is explicable on the view that the chelation of -OH and -CO.R fixes the double bonds and stabilises one of the Kekule forms; the condensation then takes place with the C atom joined to a C atom bearing the hydroxyl group by a double bond.

(I)
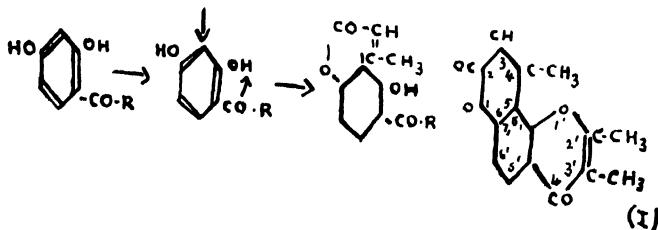
PART II—*The condensation of substituted resacetophenones with ethyl acetoacetate in presence of aluminium chloride.*

In order to ascertain the effect of constitutional factors in the condensation of resacetophenone with acetoacetic ester in presence of aluminium chloride, a study of condensation of various substituted resacetophenone derivatives was undertaken. In this part, the effect of substituents like (1) ethyl-C_2H_5, (2) bromo-Br, (3) nitro-NO_2, (4) carbomethoxy-COOMe, (5) acetyl-$COCH_3$, (6) benzyl-CH_2Ph and others present in a resacetophenone molecule has been studied.

(X = ANY SUBSTITUENT)
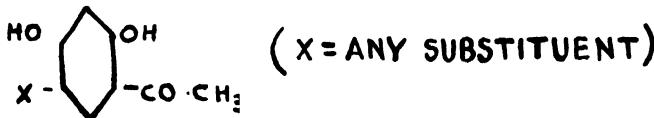
It is found that 5-ethyl- and 5-bromo-resacetophenones condense with ethyl acetoacetate in presence of aluminium chloride. The products obtained have been proved to be 5-hydroxy- 8-ethyl- and -8-bromo- 6-acetyl-4-methyl coumarins respectively ; in other cases, the condensation was not successful. The results obtained have been explained : the presence of negative groups like NO_2 de-activate the molecule, as they introduce an additional chelating factor. It may be noted that 5-ethyl- as well as 5-bromo-resacetophenone did not condense in presence of sulphuric acid.

N. M. S.

II—Some Attempts to Make out the Mechanism of Chemical Reactions : Thermal Decomposition of Nitrites.   By K. M. Mehta, Gujarat College, Ahmedabad.

With a view to elucidate the mechanism of the decomposition of nitrites in general, a detailed quantitative study of the reactions involved in the thermal decomposition of (A) Potassium Nitrite, and (B) Silver Nitrite, has been carried out.

The work has been described as under :—

Part A.—*Thermal Decomposition of Potassium Nitrite :—*

The work on the thermal decomposition of Potassium Nitrite by T. M. Oza (Ph.D. thesis, Abstract, Bom. Univ. J., 1939, p. 288) has been extended—

Section I.—Action of Nitrogen Tetroxide on Potassium Nitrite.

Section II.—Action of Nitric Oxide on Potassium Nitrite.

Section III.—Action of Nitric Oxide on Potassium Nitrate.

Part B.—*Thermal Decomposition of Silver Nitrite :—*

Section I.—Thermal Decomposition of Silver Nitrite.

Section II.—Action of Nitrogen Tetroxide on (*a*) Silver and (*b*) Silver Nitrite.

Section III.—Action of Nitric Oxide on (*a*) Silver Nitrite and (*b*) Silver Nitrate.

Section IV.—The production of Silver Oxide in the thermal decomposition of (*a*) Silver Nitrite and (*b*) Silver Nitrate.

Section V.—Action of (*a*) Nitric Oxide and (*b*) Nitrogen Tetroxide on Silver Oxide.

Experiments were conducted (*i*) at various temperatures, (*ii*) for different periods of time, and (*iii*) with varying amounts of the substance.

From the results obtained, the mechanism of the thermal decomposition of nitrites in general, and that of (A) Potassium Nitrite and (B) Silver

Nitrite in particular, has been discussed and represented as shown below :—

Thermal Decomposition of Nitrites in general—

$$2\,MNO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} M_2O + NO_2 + NO \quad .. \qquad .. \quad (1)$$

$$M_2O + NO \longrightarrow 2M + NO_2 \qquad .. \qquad .. \quad (2)$$

$$M_2O + 2\,NO_2 \longrightarrow MNO_2 + MNO_3 .. \qquad .. \quad (3)$$

$$MNO_2 + NO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} MNO_3 + NO \quad .. \qquad .. \quad (4)$$

$$M + 2\,NO_2 \longrightarrow MNO_3 + NO \qquad .. \qquad .. \quad (5)$$

$$MNO_2 + NO \longrightarrow MNO_3 + \tfrac{1}{2} N_2 \quad .. \qquad .. \quad (6)$$

$$MNO_3 \longrightarrow MNO_2 + \tfrac{1}{2} O_2 \qquad .. \qquad .. \quad (7)$$

Thermal Decomposition of Potassium Nitrite—

$$2\,KNO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} K_2O + NO_2 + NO \quad .. \qquad .. \quad (1)$$

$$K_2O + 2\,NO_2 \longrightarrow KNO_2 + KNO_3 \quad .. \qquad .. \quad (3)$$

$$KNO_2 + NO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} KNO_3 + NO \quad .. \qquad .. \quad (4)$$

$$KNO_2 + NO \longrightarrow KNO_3 + \tfrac{1}{2} N_2 \quad .. \qquad .. \quad (6)$$

$$KNO_3 \longrightarrow KNO_2 + \tfrac{1}{2} O_2 \qquad .. \qquad .. \quad (7)$$
$$\downarrow$$
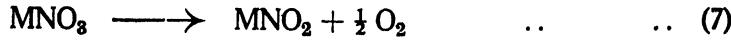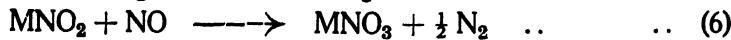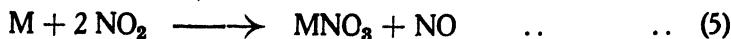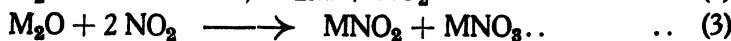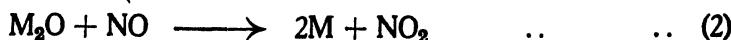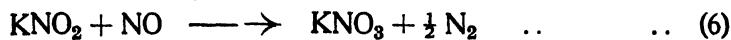
as shown in (1), (3), (4) and (6) above.

Thermal Decomposition of Silver Nitrite—

$$2\,AgNO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} Ag_2O + NO_2 + NO \quad .. \qquad .. \quad (1)$$

$$Ag_2O + NO \longrightarrow 2\,Ag + NO_2 \qquad .. \qquad .. \quad (2)$$

$$Ag_2O + 2\,NO_2 \longrightarrow AgNO_2 + AgNO_3 \qquad .. \quad (3)$$

$$AgNO_2 + NO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} AgNO_3 + NO \quad .. \qquad .. \quad (4)$$

$$Ag + 2\,NO_2 \longrightarrow AgNO_3 + NO \quad .. \qquad .. \quad (5)$$

$$AgNO_2 + NO \longrightarrow AgNO_3 + \tfrac{1}{2} N_2 \quad .. \qquad .. \quad (6)$$

$$AgNO_3 \longrightarrow AgNO_2 + \tfrac{1}{2} O_2 \qquad .. \qquad .. \quad (7)$$
$$\downarrow$$
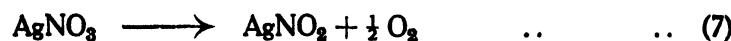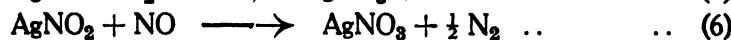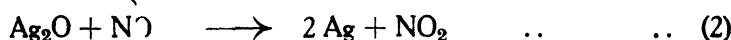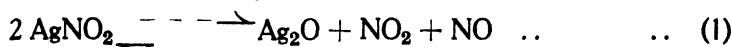
as shown in (1), (2), (3), (4), (5) and (6) above.

The difference observed in the products of the two decompositions is due to the difference in the stability of K_2O and Ag_2O towards Nitric Oxide.

SCIENCE NOTES

C-H Bond Spectrum in Relation to Molecular Structure

By

N. R. TAWDE

A S a result of the study of absorption spectra of a number of complex polyatomic molecules, we are in possession of the knowledge of vibration frequencies of different valence bonds. The C-H valency vibration being common in organic compounds, its occurrence is marked by a well-defined vibration frequency. It is expected that this, to a certain extent, would be function of the nature of the carbon compound in which its occurs. Attempt has been made in this paper to investigate this aspect with a view to see if the C-H valency vibration could enable us to classify compounds in certain well-defined molecular structures.

Kronig[*] has pointed out that the small mass of H-atom entails that the C-H bond may be said to have a rather well-defined vibration frequency in the neighbourhood of 3000 cm^{-1}. This, we see from the following table in which the known observed vibration frequencies ω of the C-H bond in absorption are recorded :

Compound	ω in cm.$^{-1}$	Compound	ω in cm^{-1}
HCN	3290	CHCl$_3$	3016
C$_2$H$_2$	3277	CHBr$_3$	3021
H$_2$CO	(2945)	C$_2$H$_4$	2988
CH$_4$	3020	C$_6$H$_6$	3030

(*Note.*—The numbers given in brackets are not known with certainty.)

At first sight the variation of frequency appears to be slight ; nevertheless, the variation is there, and it is abrupt with certain groups. We could very well arrange the frequency spectrum of the C-H valency vibration in the following groups and proceed to discuss the significance of this classification :

Group		Compound	Vibration Frequency (cm^{-1}.)
I	..	HCN	3290
		C$_2$H$_2$	3277
II	..	CH$_4$	3020
		CHCl$_3$	3016
		CHBr$_3$	3021
		C$_6$H$_6$	3030
III	..	H$_2$CO	(2945)
		C$_2$H$_4$	2988

* Kronig : Optical Basis of the Theory of Valency, Camb. U. P. 1935.

Looking to the molecules grouped under I above, we find that the frequency variation of the C-H bond in them is very slight. On the other hand the structure of these molecules, viz., HCN, C_2H_2 has been known to be of *straight linear type*.

In the group II, we have molecules of methane type, viz., methane and its halogen derivatives, as also the much discussed cyclic compound benzene. The C-H valence frequency varies only slightly from one compound to the other in this group. Except for C_6H_6, all the molecules recorded in this group are known to belong to the *tetrahedral type*. However, the frequency variation from group I to group II is large.

In the group III indicated above, we have two molecules H_2CO and C_2H_4 which are known to be *co-planar*. The atom O in H_2CO may be supposed to be replaced by CH_2 group to give C_2H_2. The frequency of the C-H valency vibration in these may be said to lie close together in a region, a little further away from the molecules of the tetrahedral type shown in group II, even though the frequency difference among molecules of group III appears to be much larger than in the other groups discussed above. But we cannot take this rigorously in view of the fact that the frequency of the C-H bond in H_2CO is not known with certainty.

It becomes apparent from the above classification, that there is likelihood that the structural characteristics of the molecules determine the nature of the valence force in the C-H bond and thus its vibration frequency. This entails that H-atom will occupy in the molecule an end-on position. If only H-atom vibrates while others are practically at rest, then the frequency of the C-H valency vibration is in some way connected with the structural characteristics of the molecule in which it occurs. The case of benzene C_6H_6 in tetrahedral type in group II above is, however, an exception. There is no other spectral evidence as to its identification with this group. But the fact that C-H frequency in it lies very close to that in the tetrahedral molecules cannot be overlooked and would require explanation, if the dependence of the C-H valency vibration spectra on the form of the molecular structure is a genuine one.

Physics Laboratories,
Royal Institute of Science,
        Bombay.

NOTES AND NEWS

Science and World 'Order

THE British Association for the Advancement of Science has organised this year, in place of the usual annual meeting, an International Conference in London between September 26 and 28 when there will be addresses and discussions on the all important subject of "Science and World Order."

World Order, New Order, Reconstruction, Planning for Peace, etc., are some of the varied names under which this subject is being discussed in the press and in different books and magazines since the last Great War and particularly during the last ten years. Under whatever name the subject is discussed they all emphasise one point, namely, that the Old Order is breaking up in all departments of life. What the New World Order is going to be like no one could say. The shape and pattern of the New Order which everybody desires today is difficult to conceive.

The educationist, the nutritionist, the economist, the architect, the planning specialist, the industrialist, the imperialist, the fascist, the communist, the socialist, etc., have each a different conception of the New Order.

As the theme for deliberation at the International Conference to be held in London is "Science and World Or 'er," the aim of the Conference is to find out what kind of World Order the Scientists have got in their mind. Whether all scientists will agree to a particular kind of World Order is a question. It is just possible that the New Order conceived of by the scientists of one country may be different from the New Order conceived of by the scientists of another country.

If the World Order was going to be one which would be acceptable to all parties concerned then it should be one which is based on *fundamental realities*. It should not be based on an incomplete concept of man or an incomplete concept of the Universe or on an inadequate conception of the relationship between man and the Universe.

The Old Order is breaking up because the form and the pattern in which it is being expressed are found to be too outgrown and rigid for the expression of the new life. We should see that the new forms we build up and the new moulds we make for the expression and unfoldment of the new phase of consciousness are such that they are of the *right* type. The new phase of consciousness will have a fuller concept of man and the Universe would consequently help one to see things in their proper perspective, to distinguish between the material, intellectual and spiritual values and to put first things first, that is, spiritual values first which emphasise unity of life, respect for life and interdependence of life, next intellectual values represented by science and finally, but by no means

to be ignored, material values represented by economics and politics. This will bring about the right adjustment and help to restore order and harmony in the world, for it would be based on the right perception of the true values of life and the proper " linking of the scientific spirit with a sense of human values."[1]

Congratulations to Dr. Bhabha

We offer our hearty congratulations to Dr. Homi J. Bhabha for the unique honour of being elected a Fellow of the Royal Society of London at the tender age of 31. We are all the more happy to note that he is the first from the Bombay University and Presidency to receive such a great distinction. Dr. Bhabha has raised the reputation of our country in the scientific world by his brilliant researches. A great future lies before him. We wish him God-speed in his noble mission in life.

A short sketch of his career is given in this issue.

D. D. K.

[1] *Nature*, 24-4-1937.

Dr. H. J. BHABHA, F.R.S.

Dr. HOMI J. BHABHA, F.R.S.

HOMI J. BHABHA was born on October 30, 1909, at Bombay, and comes from a well-known Parsi family. His grandfather, Dr. H. J. Bhabha (Senior), C.I.E., was Director of Public Instruction in the Mysore State for about twenty years and his father, Mr. J. H. Bhabha, is one of the Tata Representatives on the Council of the Indian Institute of Science, Bangalore. Bhabha was educated in the Cathedral High School of Bombay from which he took his Senior Cambridge with honours at the age of 15. Being too young to go to Cambridge, he joined the Elphinstone College and took a First Class in the F. Y. A. in 1926. He then joined the Royal Institute of Science from which he took the I.Sc. of the Bombay University in the First Class in 1927. He was made a scholar of the Royal Institute of Science. Dr. Bhabha's name stands engraved in the List of Honour at the entrance of the Royal Institute of Science.

From his earliest days in the College, he took a very keen interest in Theoretical Physics, and he had studied Einstein's Theory of Relativity at about the age of 15. In his younger years, he was also very mechanically inclined, and much against his will, he was prevailed upon to take a degree in Engineering in Cambridge. He took his B.A. in the Mechanical Science Tripos at Cambridge in the First Class, and having achieved a good professional degree, he was allowed to change over to Theoretical Physics—his first love. His performance in the Mechanical Sciences Tripos was an outstanding one for many years, having taken advanced papers in six special subjects, of which it is necessary only to take three. He was a scholar of Caius College, and in view of the brilliant First Class obtained by him, he was given studentships by the College in 1930 and 1931 to enable him to study advanced Mathematics and Theoretical Physics. His foundation of Modern Theoretical Physics was laid in these two years under Professors P. A. M. Dirac and N. F. Mott.

In 1932 he was awarded the Rouse Ball Travelling Studentship in Mathematics from Trinity College and spent 1932–33 at Zurich working under Professor W. Pauli, when he wrote his first paper " Zur Absorption der Hohenstrahlung " at the end of that period. In 1933–34 he worked with Professor E. Fermi at Rome and with Professor H. A. Kramers at Utrecht and in 1936–37 spent five months at Professor Niel Bohr's Institute of Theoretical Physics at Copenhagen.

He had already been awarded the Isaac Newton Studentship in 1935 for three years, and in 1937, he was awarded the senior studentship for Great Britain of the Exhibition of 1851, which he held for three years. He is the only Indian to have had this distinction.

From 1935 until 1939, when the outbreak of war prevented his return to England, Dr. Bhabha had been lecturing at Cambridge on Cosmic Radiation, Nuclear Physics and Relativistic Quantum Mechanics

(besides giving the usual elementary courses on electricity and magnetism). In October 1937, at the invitation of Professor Max Born he gave a course of lectures on cosmic radiation at Edinburgh.

In 1939 the Royal Society decided to finance him out of the Mond Fund to act as Theoretical Physicist to Prof. Blackett's School of Cosmic Ray Research at Manchester and to enable him to carry on his own work at Manchester and Cambridge. He was also invited to attend the Solvay Conference at Brussels which was to have been held in the October of 1939, but was prevented by the outbreak of war.

He came out frequently during the summer vacations to India and it was while on one of these holidays that the war broke out and prevented his return to England. Since then he has carried on his own research at the Indian Institute of Science, Bangalore.

It will be seen from the above short account, that Dr. Bhabha has had the privilege of coming into contact with the best brains in Theoretical Physics. " Cosmic Ray " investigations have proved extremely far-reaching in recent years and for getting further knowledge of the ultimate constitution of matter, Scientists have travelled all over the Globe from almost the North Pole to the South, and have sent their measuring instruments from the deepest accessible depths in mines and lakes to a height of 28 kilometers which is practically the top of the atmosphere. In Dr. Bhabha India is now in a fortunate position of having one of the foremost successful interpreters of this important phenomenon ; he has also a fine batch of workers at Bangalore and several workers at Calcutta (in the Bose Research Institute and the University College of Science). It would be quite feasible to have a cosmic ray research scheme, in which all the workers could undertake co-operative research as in the U. S., under the guidance of Dr. Bhabha.

Dr. Bhabha was awarded the Fellowship of the Royal Society which itself is an obvious appreciation of his eminence in original investigations. The earliest age at which the F. R. S. has been conferred on an Indian is 31, when in 1918 Ramanujam was made a Fellow of that Society. Bhabha today has equalled that record, being only 31 when he was elected.

Dr. Bhabha is a very competent painter and his pictures excited the interest of Roger Fry who tried to induce him to take to painting as his profession. He has designed scenery for several productions of operas and plays in Cambridge. The scenery for Mozart's Idomeneo attracted much attention and photographs of the settings were given in the illustrated journals of England, such as the " Sketch," etc. In fact, it was planned to reproduce this opera on the London stage under an internationally famous conductor, and Dr. Bhabha was again asked to design the scenery. The outbreak of the war put an end to this project.

G. P.

BOOK REVIEWS

(A Guide to) Circular Protractor with Sixteen Special Points. By N. R. Tamhankar, Vidyapeetha, Kolhapur, 1940; (with the Circular Protractor).

This is a pamphlet of 10 very small pages, explaining the use of the Circular Protractor invented by the author. The protractor is a thin circular cardboard disc, with the circumference marked in degrees. Twelve selected points are marked on the circumference, and four others including the centre are punched through the disc. By joining various sets of three or more points from these, various figures—such as perpendicular lines, parallel lines, regular polygons, equilateral triangles, figures commonly used to prove the concurrency theorems, etc.—can be obtained. In short it is a compact stencil for drawing geometrical figures.

The author in his preface claims that the protractor would be helpful to students in understanding geometry and in constructing accurate figures; while Prof. V. V. Naralikar (a former pupil of the author) commends its use in a foreword. We are however unable to share the enthusiasm of either, as we feel that a proper use of the ordinary geometrical instruments would be simpler for the accurate construction of figures, as also more effective to acquire mastery of geometrical theory, than the use of this protractor. The price is not mentioned, but considering that it is made of thin cardboard, it should be within the reach of the poorest student.

K. R. G.

General Physics. By W. L. Whiteley; Published by the University Tutorial Press, London, 1940. Price 7s. 6d.

Introduction of modern teaching methods have necessitated a re-alignment in the writing of text-books for schools. This book on general physics intended for university matriculation course has been written by one intimately connected with the teaching of the subject. As such, the orientation given by the author in approaching the subject in the light of his experience, is the presentation of the fundamentals in more or less assimilable form. This is evident from the inclusion in the book, of the many phenomena and things of common occurrence by way of illustration, in order to make the subject intelligible and interesting. The subject matter is adjusted to the normal needs of matriculation standard and contains typical numerical problems worked out at each stage of theory, along with model exercises for practice. The book is a welcome addition to the list of school texts and deserves a trial.

N. R. T.

Chemical Analysis of Kolhapur Waters. By J. W. Airan and S. V. Shah ;
    Published by the authors at Kolhapur.

The pamphlet under review deals with the chemical analyses of a large
number of samples of water derived from different sources in the vicinity
of Kolhapur. The data collected have enabled the authors to draw
some provisional conclusions regarding the suitability of various sources
of water supply at Kolhapur for drinking purposes. The authors have
made an interesting suggestion that chemical analysis of water by itself
without the corresponding bacteriological examination may serve as
a rough guide to the quality of potable waters. This is only a tentative
suggestion but it would be interesting if the authors could collect more
relevant data with a view to test the validity of this suggestion.

R. C. S.

Milk (in Gujarati). By Dr. N. M. Shah, M.Sc., Ph.D., Lecturer in
    Chemistry, Gujarat College, Ahmedabad, Illustrated ; Published by
    the Gujarat Vernacular Society, Ahmedabad. Price 6 annas.

There are very few books published in Gujarati on foodstuffs embodying
the results of the latest scientific investigations on them. We, therefore,
welcome this book on Milk written in Gujarati and recommend it with
pleasure to the Gujarati-speaking public as they will read it with profit
not only to themselves but also to their children. The book contains
many diagrams and tables and treats of milk, milk products and other
allied subjects. It also gives comparative values of different foodstuffs
with milk. There is a chapter on the question of vegetarian and non-
vegetarian diets, also one on tea, coffee, cocoa and tobacco, and another
on the comparative merits of milk and alcohol as drinks.

In the next edition of the book we would suggest the author to give
the quantities in household measures such as a teaspoon, a tablespoon,
a cup and so on instead of in grams and litres.

D. D. K.

Radio Physics Course. By Alfred A. Ghirardi, E.E. Second Edition,
    revised and enlarged, Eighth Impression, 1937 ; Published by the
    Radio and Technical Publishing Co., N. Y., U. S. A. Price 4 dollars.

Since the advent of radio as a means of entertainment and a vehicle
of long-distance communication, public interest in it has grown so rapidly
that informative popular literature on the A, B, C of the science of radio
came much in demand. The present *Radio Physics Course* by Ghirardi
is the culmination of it and marks a distinct attempt at satisfying the
want of those, who even without the background of higher physics desire

to master the technique of it and make it their career. The author starts by introducing the physics of sound and electricity in a popular way and develops the subject by successive easy steps into a separate branch of engineering. The treatment is such that it aims at making the student of radio course, an expert hand for service in various types of radio establishments—public, commercial and industrial. Only those who apply themselves seriously to the study of radio technique can appreciate the intelligent and systematic work of the author in producing this volume. It will serve as an excellent text-book in radio-schools.

N. R. T.

Modern Radio Servicing. By Alfred A. Ghirardi, E.E. First Edition, 1935, Second Impression, 1936; Published by the Radio and Technical Publishing Co., N. Y., U. S. A. Price 4 dollars.

This is an indispensable book to all service men in the radio profession. It is a compilation that can serve as a reference book, dictionary and guide to all engaged in the practise of radio engineering and radio equipment. It contains up-to-date useful information, inclusive of the items that grow from day to day as a result of progress in this new and expanding branch of science and technique.

N. R. T.

Radio Trouble-Shooters' Hand-Book. By Alfred A. Ghirardi, E.E. First Edition, 1939; Published by the Radio and Technical Publishing Co., N. Y., U. S. A. Price 3 dollars.

In this very valuable book written as a companion to *Modern Radio Servicing,* the author has undertaken a very stupendous task of compiling practical data that will save enormous time of radio repairers. Component parts of a radio model have their own characteristics and these together make up for the efficiency and durability of the model. In case trouble arises, it has to be traced to one or more of these parts. Proper diagnosis of the trouble is a preliminary to its treatment at the hands of a repairer or serviceman. In order to help this diagnosis, " case histories " are collected in this volume along with the common troubles which a radio mechanic ought to be familiar with. Useful charts, circuits and essential numerical constants are supplied for ready reference. They will always be found handy by radio serviceman. In all these, the author confines himself to radio equipment of American origin probably to limit the scope of the publication. The idea of the immensity and complexity of the material compiled in the book can be gathered by perusing through its pages. It should be a treasure possession both to the radio technician and businessman.

N. R. T.

Table showing M.Sc., M.Sc. (Tech.) and Ph.D. theses accepted in Physics, Chemistry and Geology (from July, 1940 to September, 30, 1941)

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
	M.Sc.		
	Physics—		
Kathavate, Y. V.	Application of the photo electric cell to the study of light flashes effusion phenomena in a degenerate Bose-Einstein Gas.	Professor D. V. Gogate	B.C.
Vaswani, J. P.	Distribution of Scattered X-Rays	Professor S. G. Khubchandani	D. J. S.
	Chemistry—		
Advani, R. D.	Alkaline Electrometric titrations of soluble proteins in presence of sugars—I, gelatin.	Professor C. S. Narwani	D. J. S.
Badami, P. L.	Physico-chemical changes in the Mandya soil	Dr. Mata Prasad	R. I. Sc.
Bavdekar, P. R.	Photo-reduction of alcoholic solutions of ferric chloride in artificial light	Dr. Mata Prasad	R. I. Sc.
Bhatt, P. V.	Studies on 6-acetyl-4 methyl umbelliferone	Professor D. B. Limaye	R. I. E. I.
Chitre, M. K.	Manufacture of Hydrogen peroxide	Dr. Mata Prasad	R.I.Sc.
Deliwala, C. V	Studies in Coumarins	Dr. N. M. Shah	G.C.
Desai, T. V.	Studies in Gels	Dr. Mata Prasad	R.I Sc.

Author	Thesis	Supervisor	Institution
D'Souza, J. P.	Studies in Emulsions	Dr. B. K. Vaidya	U.D.C.T.
Cogate, V.S.	Capacity changes in the gel forming mixtures during setting	Dr. Mata Prasad	R. I. Sc.
Bapat, N.V.	1. Preparation of 6-hydroxy-3-methyl coumarone from the ethyl ether of 4-methyl-umbelliferone. 2. Synthesis of 4-hydroxy-3-methyl-coumarone (a homokaranjol) from 5 hydroxy-4-methyl coumarin. 3. Extension of the Nidhone process for the synthesis of 2 acyl-resorcin to 4-propyl resorcin.	Professor D. B. Limaye	R. I. E. I.
Damaney, C.P.	1. Electrometric measurement of the rate of oxidation of ferrous tannate in presence of various acids. 2. Electro-conductometric titrations of mixtures of sodium carbonate and sodium bicarbonate. 3. Preparations of pure sodium bicarbonate simultaneously from natural soda deposits in Khairpur State by electrolysis.	Professor C. S. Narwani	D. J. S.
Gurshani, G. T.	Rhythmic precipitation of AgCl in gelatin tanned with CrCl3. Base exchanges of Hg ions absorbed on wool and influence of Formaldehyde on the reaction of HgCl2 with wool.	Professor C. S. Narwani	D. J. S.
Hutchins, W. A.	Studies in chalkone oxides and flavones from chalkone dibromides	Dr. T. S. Wheeler and Dr. R. C. Shah.	R. I. Sc.
Jatti, V. V.	Studies in Coumarins	Dr. R. C. Shah	R. I. Sc.
Joglekar, R. V.	Catalytic Hydrogenation of Oils	Professor S. K. Kulkarni-Jatkar	I. I. Sc.
Joshi, R. H.	X-Ray analysis of crystals of p-acetanisidide and acetanilide and methylacetanilide and magnetic anisotropy of these crystals.	Dr. Mata Prasad	R. I. Sc.
Kamat, R. K.	Reactivity of some phenyl benzyloxystyryl ketone dibromides.	Dr. T. S. Wheeler and Dr. R. C. Shah.	R. I. Sc.
Kailash, B. N.	Condensation of chalkones with compounds containing reactive methylene group.	Dr. R. C. Shah	R. I. Sc.

M.Sc.

Chemistry—contd.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
Kulkarni, D. R.	Studies in Coumarins	Professor R. L. Alimchandani	K. C.
Mehta, B. S.	Synthesis of μ Keto butyric acids with methoxy phenyl groups as substituents in ∝ and μ positions.	Dr. K. S. Nargund	G. C.
Mehta K. M	Some attempts to make out the mechanism of chemical reactions. thermal decomposition of nitrites.	Professor M. S. Shah	G. S.
Mohammed. S. H.	Synthesis of tetrahydro naphthalene derivatives from chalkones	Dr. R. C. Shah	R. I. Sc.
Nagamani Shamarao (Miss).	1. Studies in Binary Mixtures. 2. *Dispersion* of dielectriccone constant of organic liquids.	Professor S. K. Kulkarni-Jatkar	I. I. Sc
Nagarkar, V. V.	1. Synthesis of 3 3-dimethyl-6. 7-furo coumarone. 2. Synthesis of 3-methyl-7 8-furoflavone 3. Synthesis of 2 4: 6-triacetyl-resorcin.	Professor D. B. Limaye	R. I. E. I.
Naimpally, R. B.	Studies in Colloids	Dr. S. C. Devadatta	W.
Nathan Abigail (Miss)	The effect of Hydrogen Ion concentration on the setting of thorium Phosphate Gels.	Dr. Mata Prasad	R. I. Sc.
Parakh. T. C.	1. Influence of sugars on the size-frequency of particles of protein protected emulsions. 2. Influence of metallic salts on the size frequency of the particles of protein protected emulsions.	Professor C. S. Narwani	D. J. S.

Patwardhan, N. K.	Studies in the physico chemical changes in black cotton soil during nitrification.	Dr. Mata Prasad				R. I. Sc.
Rege, N. D.	Sugars and Minerals in Bombay Fruits	Professor S. C. Devadatta				W.
Shetgeri, V. N.	Heterogenous reaction between chromium sulphate and manganese dioxide.	Dr. Mata Prasad				R. I. Sc.
Shirsat, M. V.	Studies in Amidines	Dr. R. C. Shah				R. I. Sc.
Ullal, V. V.	Studies in the chromone series, "Transformation of aroyloxy-acetoarones into o-hydroxy diaroylmethanes and the synthesis of flavones from o-diaroylmethanes."	Dr. R. C. Shah				R. I. Sc.
Viswanath, C. V.	Studies in Organic Gels	Dr. Mata Prasad				R. I. Sc.
Vyas, V. A	Synthetical anthelmentics	Dr. K. S. Nargund				G. C.

Geology—

| Agashe, L. V. | A study of rocks occurring near Murgad in the Parasgad Sub-division of the Belgaum District. | Professor K. V. Kelkar | | | | F. C. |
| Patankar, W. P. | A study of rocks in the neighbourhood of Ramgarh and Kankavt. | Professor K. V. Kelkar | | | | F. C. |

Technology—

| Pai, M. U. | Study of High Sulphur Indian Coals | Dr. M. R. Mandlekar | | | | U. D. C. T. |
| Pandit, M. G. | The influence of nitrogen peroxide on the spontaneous ignition of mixtures of diethylether with oxygen. | Dr. G. P. Kane | | | | U. D. C. |

Ph.D.

Name of the Candidate		Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
		Physics—		
Patankar, V. S.	..	The intensity distribution among the 1st and 2nd positive band system of the N_2 molecule.	Dr. N. R. Tawde	R. I. Sc.
		Chemistry—		
Bokil, K. V	..	Synthesis in the Chaulmoogric acid series	Dr. K. S. Nergund	G. C.
Desai, C M	.	Action of light on some organic colouring matters	Dr. B. K. Vaidya	U. D. C. T.
Iyer, B H.	..	Dihydroresorcinols : 1. studies with methone 5 5-dimethyldihy-droresorcin and its derivatives 2. attempts towards synthesis of cantharidin.	Dr. P. C. Guha	I. I. Sc.
Jagdish Shankar	..	Molecular Orientations in crystals of organic compounds from their x-ray and magnetic data and magnetic anisotrophy of the "Formate group	Dr. Mata Prasad	R. I. Sc.
Limaye, S. D	..	1. A critical examination of Agarwal and Dutt s paper on synthetic coumarins—coumarins derived from resacetophenone 2. Extension of the Nidhone Process for the synthesis of 2-acyl–resorcins to 2-acyl-4-alkyl-resorsins and further papers on Nidhone process etc. in all 9 papers	Professor D B Limaye	R. I. E. I

Mankar, B. N.	Relation between absorption spectra and chemical activity in the ultra violet and of the derivatives of aceto aretic acid.	Dr. R. K. Trivedi	B. C.
Nadkarni, D. R.	1. Synthesis of naturally occurring substances relating to chalkones. 2. Flavone derivatives from glycerol ethers of resacetophenone.	Dr. R. C. Shah	R. I. Sc.
Panse, T.	Studies in Coumarones and Coumaranones	Dr. R. C. Shah	R. I. Sc.
Shah, M. P.	Light absorption in the ultra-violet; chemical constitution and chemical activity of some derivatives of aceto acetic acid series.	Dr. R. K. Trivedi	B. C.
Majmudar, R. N.	Lake Pigments	Professor K Venkatraraman	U. D. C. T.
Shah, H. A.	Y—substitution in the Resorcinol Nucleus	Dr. R. C. Shah	R. I. Sc.
Vaidya, R. M.	1. A spectroscopic study of light absorption by some solutions and dyed gelatine and cellophane films, for the preparation of various types of light filters. 2. Construction of a compensated photo electric reflection meter for the measurement of whiteness and lustre.	Dr. P. K. Vaidya	U. D. T. C
Technology—			
Bhat, R. V.	Studies in the Naphtol AS series	Professor K. Venkataraman	U. D. C. T.
Gandhi, R. C.	Antiseptics in Textiles	Professor K. Venkataraman	U. D. C. T.
Kedva, K. G.	Coloured and Modified Cements	Professor K. Venkataraman	U. D. C. T.

BOOKS RECEIVED

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Annual Report of—

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The Indian Association for the Cultivation of Science, for the year 1940.

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Announcement of the College of Engineering, Civil, Mechanical, Electrical, Chemical and Administrative Engineering for 1941–42, Vol. 32, No. 13. Published by the Connell University, New York.

Deco Trefoil, June 1941.

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A CYTOLOGICAL STUDY OF THE GENUS ANONA

By

L. S. S. KUMAR AND MRS. KAMAL RANADIVE,

Botany Department, College of Agriculture, Poona

INTRODUCTION

THE natural order Anonaceæ includes many plants of economic importance and the most outstanding of these belong to the genus *Anona*. While the closely allied orders Ranunculaceæ, Magnoliaceæ and Nymphæaceæ have been investigated by several workers, very little attention has been paid to Anonaceæ. Sorokin (1927) has described the cytology and morphology of several geographical races of *Ranunculus acris*. Langlet (1927) has determined the chromosome numbers of many genera belonging to Ranunculaceæ. Langlet and Andrews (1929) have also studied some genera of the Nymphaeaceæ and Magnoliaceæ. The only work on *Anona* appears to be that of Juliano (1935) on the megasporogenesis in two species. The present cytological study was undertaken to find out the inter-relationship between the different species belonging to *Anona* and also the relation of the genus to allied genera and natural orders.

MATERIAL AND TECHNIQUE

Four species of *Anona* have been used for the present study. They are : *A. squamosa*, *A. reticulata*, *A. muricata* and *A. cherimola*. All the four are cultivated garden plants and bear edible fruits. *A. squamosa*, commonly known as the custard apple, is a tropical plant, cultivated all over India for its sweet pulpy fruit. *A. reticulata*, the common " bullock's heart," is also cultivated in many parts of India, though not so extensively as *A. squamosa*. *A. muricata* (Soursop) and *A. cherimola* (Cherimoya) are found only very rarely in India.

The material for cytological examination was all collected from gardens in Poona and Kirkee. Anthers from buds of the proper stages for

studying meiosis, as determined by temporary acetocarmine smears, were fixed in Nawaschin's fluid or McClintock's mixture and then stored in 70 per cent. alcohol. The usual smear technique did not succeed as the pollen mother cells are in a single row in each loculus of the anther and considerable pressure has to be used to smear them evenly. Moreover, the pollen mother cells did not properly stick to the slides. So, after some trials, a modified technique, described below, was adopted with success. Few anthers stored in 70 per cent. alcohol were teased in a drop of clear water on a clean slide. The anther walls and other unnecessary tissues were completely removed. The drop of water containing the pollen mother cells were then carefully transferred to a second clean slide on which a thin smear of liquid paraffin was previously applied. The slide was allowed to dry over-night. The next day, all the pollen mother cells were found to adhere fast to the slide. The slide was then stained in iron-alum-hæmatoxylin. Sections were cut from material fixed in Nawaschin's fluid and stained in gentian violet or hæmatoxylin. Both, sections and smears gave satisfactory preparations.

MICROSPOROGENESIS

ANTHER DEVELOPMENT

The early development of the anther is in the usual manner. The primary sporogenous layer gives rise to only one row of pollen mother cells in each loculus of the anther and so in cross sections (Fig. 1) we find only one pollen mother cell in each loculus. This single p. m. c. is surrounded by a layer ot tapetal cells.

MEIOSIS

Meiosis was studied in detail in four species of *Anona*. As the general course of meiosis is the same in all the four, for the sake of brevity, the description refers particularly to *A. squamosa*, while differences observed in the other species are mentioned.

(a) *Resting stage.*—After the formation of the pollen mother cells from the primary sporogenous layer, the nucleus in each cell increases in size along with an increase in size of the cell. After some increase in the dimensions of the cell, the growth of the cell stops, while the nucleus continues to enlarge and enters meiotic division.

(b) *Lepto-zygotene.*—The coiled structure of the chromatin threads and their uniform distribution throughout the nuclear cavity are seen clearly at leptotene stage. A large, deeply staining nucleolus is seen within the tangle of chromatin threads. In *A. muricata* nucleolar budding is a very common phenomenon. Forty-five out of fifty pollen mother cells examined at early prophase exhibited this feature. In *A. cherimola* also this is noticed and in most cases the nucleolar bud separates from the large nucleolus and thus nucleoli of unequal size are frequently seen. In the other two species, this is observed only rarely. Sorokin (1927) states that the presence of dividing nucleolus or two separate nucleoli is

an outstanding character in many races of *Ranunculus acris*. In all the species of *Anona* examined, a network of chromatin threads is seen in the nuclei at early leptotene. Zygotene pairing usually commences near the ends of chromosomes (Fig. 2). The exact number of chromosomes is difficult to count at this stage. However, 12 to 14 chromosomes could be counted in *A. muricata*, and 6 to 7 pairs in *A. cherimola* and *A. reticulata*. In these species the ends of chromosomes appear a little swollen and knob-like, and this helps in counting the number. But in *A. squamosa* the chromatin thread is more slender and there is no specialised appearance at the end. In all the four species, one or sometimes two pairs of chromosomes appear to be in contact with the nucleolus.

(c) *Pachytene* stage was observed only in a few nuclei. But this stage appears to be easily passed over and the very close association of the chromosomes into bivalents was rarely observed.

(d) *Diplotene.*—In *A. squamosa* at early diplotene (Fig. 3) the bivalents show the major spirals clearly. Interstitial chiasmata are more frequently seen than terminal ones. The total number of chiasmata gradually decreases from early to late diplotene due to terminalisation. This terminalisation of chiasmata was studied in *A. squamosa, A. muricata* and *A. reticulata*.

(e) *Diakinesis.*—Even at diakinesis, the nucleolus is faintly visible and one bivalent is usually seen in contact with it in all four species (Figs. 4, 11, 13 and 14). In most of the cells at late diakinesis, there is only a single chiasma in each bivalent. (The figures are drawn more to show the relative size of bivalents than the typical chiasma frequency). In *A. cherimola* a marked precocity is seen in the separation of some bivalents into univalents even before metaphase stage. Forty to fifty nuclei at diakinesis were studied in each species and it was found that with one or two exceptions, there are seven bivalents in each nucleus. So the diploid number in each species should be 14. No trivalent or tetravalent association was seen at diakinesis or first metaphase, though due to precocious separation a few univalents were found.

In *A. squamosa* and *A. muricata* one bivalent each is attached to the nucleolus, while in the other two species in addition to the bivalent attached to the nucleolus it was possible to make out another satellited bivalent in a few cells. (See Fig. 13, *A. cherimola*.)

(f) *Metaphase.*—In all the four species, seven bivalents (or in some cases in *A. cherimola*, a few bivalents and a few univalents, giving a total of 14 chromosomes) were seen at metaphase.

(g) *I. Anaphase.*—The anaphasic separation is uniform and balanced in all the bivalents. No case of chromatid bridge formation was observed.

Both in *A. muricata* and *A. squamosa* the equational split that is ordinarily seen at the second division is seen during the first anaphase itself. Each chromosome appears double due to the diverging of the chromatids from each other. This diverging of the chromatids is due

to each chromatid developing its own matrix and thus separating into two instead of being enveloped by a common matrix. In *A. reticulata* at the first anaphase only rarely we find the chromatids separate in each chromosome. In *A. cherimola*, which has smaller chromosomes, this separation is not observed at all till the second metaphase. Those chromosomes which have median or sub-median attachment constrictions are X-shaped, while those with terminal or sub-terminal constrictions are V-shaped.

(*h*) *Telophase*.—The seven chromosomes could be easily counted in favourable cells. One of the seven is usually seen attached to the nucleolus.

(*i*) *Second Division*.—The second division rapidly follows the first. The chromosomes contract much further and arrange at the equatorial plane. Unlike the usual condition in dicots, where one spindle is at right angles to the other, here both lie in the same plane (Fig. 7). As the chromatids had already separated at the first anaphase, except at the kinetochore, the second division involves only a separation of the chromatids at this region also. The investigations of Matsuura and Haga (1940) have shown that the failure of the functionally double kinetochore to separate at the first division is one of the important structural differences distinguishing meiosis from mitosis. In *A. cherimola*, as stated earlier, the chromatid separation becomes visible only in the second division. But this may be due to the smaller size of the chromosomes of this species.

(*j*) *Cell Division*.—Cell division takes place by furrowing of the cytoplasm (Figs. 6-9). At the first telophase itself two furrows appear at opposite ends in the cytoplasm. This is completed only by second telophase, when two furrows appear in the middle of each daughter cell in a plane at right angles to the first and thus four daughter cells each containing one daughter nucleus are formed.

(*k*) *Irregularities*.—Precocious separation of bivalents in *A. cherimola* has already been mentioned. Besides this, fragmentation of chromosomes is observed in *A. muricata* and *A. reticulata*. In the former, one to four fragments are observed at diakinesis in a few cells. Sometimes these fragments are scattered in the cytoplasm and are generally lost in the first division itself.

DISCUSSION

Chromosome number and phylogeny.—The present study has shown that four species of *Anona*, having very distinctly different morphological features have the same haploid chromosome number, namely seven. The basic numbers of chromosomes of many genera belonging to allied natural orders have been determined by previous workers. The nuclear behaviour in *Anona* is very similar to what has been described by Sorokin (1927) in *Ranunculus acris*, which has also seven as the haploid number. Some geographical races and gynodimorphic forms of *Ranunculus acris* show $2n=12$ and $2n=18$ and also intermediate numbers (Sorokin, 1927). Langlet's (1927) observations show that the Ranunculaceous genera

could be classified into three groups based on three basic numbers of chromosomes, 6, 7 and 8. Whitaker (1933) has grouped Magnoliaceæ into two, with basic numbers 14 and 19. The genera *Illicium*, *Kadsura* and *Eupleta* have 14 as haploid number—a multiple of 7. Several genera of the Ranunculaceæ like *Ranunculus*, *Leptopysum*, *Cimcifuga*, *Anemone* and *Aquilegia* have seven as the haploid number of chromosomes, while *Thalictrum* shows a polyploid series with seven as the basic number. This clearly shows the close affinity of *Anona* to these genera. In the genus *Anona* itself, a comparative study of chromosome size, morphology and behaviour at first division points out that *A. squamosa* and *A. muricata* fall into one group, while *A. cherimola* falls into another with *A. reticulata* as an intermediate type.

The observation of seven as the basic number of chromosomes in *Anona* is of some interest in connection with Anderson's (1934) speculations on the origin of angiosperms. Relying mainly on the observations of Whitaker (1933) that the basic chromosome number in the Magnoliales, a very primitive group of angiosperms, is 19, Anderson has suggested that the angiosperms may have originated in part at least from wide crosses between some of the members of the seven chromosomed and twelve chromosomed gymnosperms. Based on their studies on the Menispermaceæ, an order allied to the Magnoliales, Joshi and Rao (1935) have stressed Anderson's suggestions and have drawn attention to the presence of haploid numbers with a progressive difference of seven in the Menispermaceæ. This further indicates phylogenetic affinity between Magnoliaceæ, Anonaceæ and Menispermaceæ, all considered primitive angiosperm groups on account of their floral structures. So far as chromosome *numbers* suggest any phylogenetic relationship (when taken along with morphological characters), is it not possible that the Ranunculaceæ and Anonaceæ which have a basic chromosome number of 7, originated from an ancestral genus with seven as basic number and which also would have given rise to the 7-chromosomed Gnetales ?

SUMMARY

1. Microsporogenesis in four species of *Anona*, viz., *A. squamosa*, *A. muricata*, *A. reticulata* and *A. cherimola* is described.

2. The haploid chromosome number in all the four species is seven.

3. Nucleolar budding and occasionally division to form two nucleoli occur in *A. muricata* and *A. cherimola*.

4. One bivalent at the first division and one chromosome at the second division are usually found associated with the nucleolus.

5. In *A. muricata* and *A. squamosa* the component chromatids of each chromosome become distinctly separated at I Anaphase itself. In *A. reticulata* this feature is rarely observed and in *A. cherimola* it becomes manifest only at second division.

6. Based on cytological observations it is shown that *Anona* is closely related to some genera of Ranunculaceæ which natural order is considered closely allied to Anonaceæ on morphological grounds.

7. The suggestive significance of the haploid number seven in *Anona*, in the light of Anderson's (1934) observation is pointed out.

The authors wish to thank Mr. A. Abraham, Assistant Cytologist, for his help in the preparation of the diagrams and in writing the paper.

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Explanation of Figures

All figures in Plates I and II were drawn with the aid of a Leitz Camera lucida from permanent preparations of *Anona* stained in hæmatoxylin.   The original magnification of Figure I is X 320 and of all the other figures is X 1,500.   Reduced in reproduction to about half of the original in Plate I, and to about three-fourth of the original in Plate II.

PLATE I—ANONA SQUAMOSA
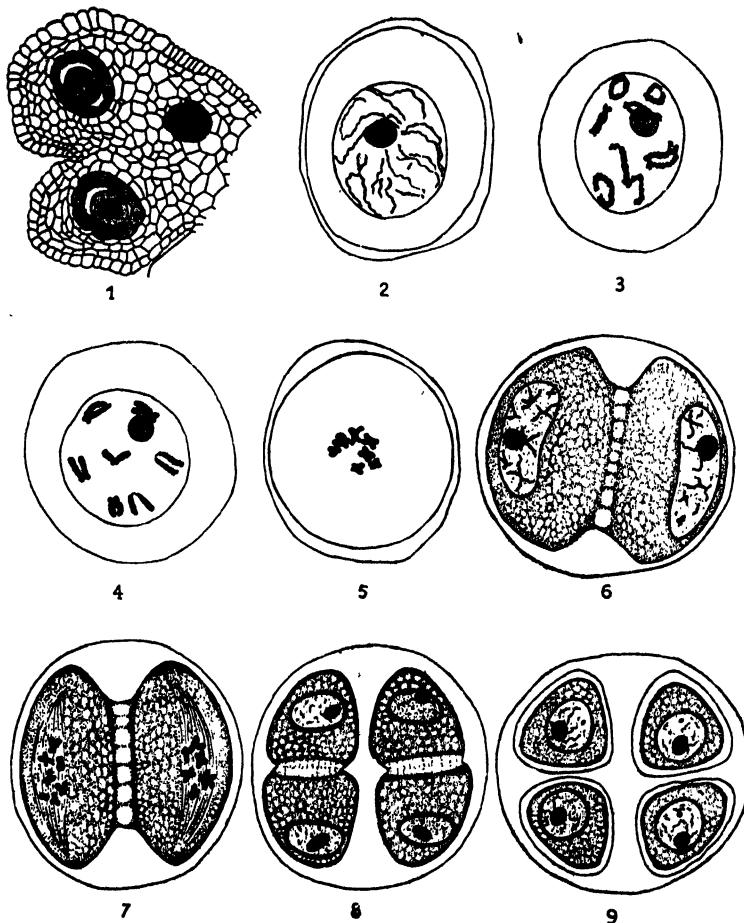
FIGURE 1.—One-half of cross section of an anther showing single pollen mother cell in each loculus surrounded by tapetal cells. The shaded cells on the right are secretory cells.

FIGURE 2.—Lepto-zygotene. Pairing of chromosomes commenced at the ends.

FIGURE 3.—Diplotene, showing seven bivalents, one of which is attached to the nucleolus.

FIGURE 4.—Diakinesis showing reduction in number of chiasmata.

FIGURE 5.—Metaphase. Close grouping of bivalents.

FIGURE 6.—II Prophase. The diverging chromatids of the seven chromosomes are clearly seen. Commencement of furrowing of cytoplasm.

FIGURE 7.—II Pro-metaphase. Seven chromosomes en each spindle. The structurally double nature of each chromosome is clearly seen.

FIGURE 8.—II Telophase. Later stage in cell division. Two cells are formed and commencement of division of the daughter cells is seen.

FIGURE 9.—Tetrad stage.

PLATE II

SOME PARASITIC NEMATODES OF FISHES—I

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THE present paper is based on material collected by the writer on several occasions from the freshwater fishes of Poona, as also on a part of the material very kindly sent by Dr. G. D. Bhalerao of Muktesar.

Out of the eleven forms recorded here, seven appear to be new, two already described and two undetermined. Their systematic positions are given below. The scheme of classification adopted by Baylis in the two volumes on Nematoda in the Fauna of British India series, is followed here.

Family Ascaridæ Cobbold, 1864

Genus Raphidascaris Railliet and Henry, 1915

Raphidascaris sp.

Family Kathlaniidæ Travassos, 1918

Genus Spironoura Leidy, 1856

Spironoura khadrai n. sp.

Family Quimperiidæ Baylis, 1930

Genus Gendria Baylis, 1930

Gendria brevispiculum n. sp.

Genus Paraquimperia Baylis, 1934

Paraquimperia anguillæ n. sp.

Genus Metaquimperia nov.

Metaquimperia callichroi n. sp.

Metaquimperia bagarii n. sp.

Family Spiruridæ Örley, 1885

Genus Heliconema Travassos, 1919

Heliconema ahiri, n. sp.

Family Camallanidæ Railliet & Henry, 1915

Genus Camallanus Railliet & Henry, 1915

Camallanus ophicephali Pearse, 1934

Genus Procamallanus Baylis, 1923

Procamallanus mehrii Agarwal, 1930

Procamallanus sp.

Genus Paracamallanus Yorke & Maplestone, 1926

Paracamallanus ophiocephali n. sp.

Family ASCARIDÆ Cobbold, 1864

Raphidascaris sp.

Four immature females, apparently belonging to this genus were obtained from the body cavity of *Anguilla bengalensis*. The œsophagus gives out a small ventriculus from which arises a posteriorly directed appendix, the terminal portion of which bends and forms a loop.

Family KATHLANIIDÆ Travassos, 1918

Spironoura khadrai n. sp.

A large number of these parasites was obtained from the intestine of a freshwater fish *Barbus dobsoni*. The male measures 7·15 to 14·25 mm. in length and has a maximum thickness of 0·56 to 0·872 mm. Its posterior end is curved ventralwards. The female is straight, 12·4 to 13·0 mm. long and has a maximum width of 0·575 to 0·6 mm. The transverse cuticular striations are fine.

The head is globular but in some specimens it appears to be somewhat flattened antero-posteriorly. Its diameter is 0·144 to 0·181 mm. in the male and 0·16 to 0·165 mm. in the female. Each lip bears a small forwardly directed tooth-like projection. The oral cavity is 0·06 to 0·07 mm. and is surrounded by a cuticular ring.
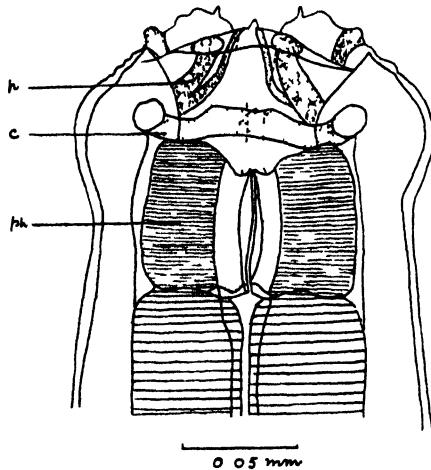
FIG 1

Spironoura khadrai: Anterior end of male, dorsal view. c, cuticular ring;
p., forked papilla, ph, pharynx.

The entire œsophagus including the posterior bulb is 1·871 to 2·208 mm. long in the male and 1·925 to 2·17 mm. in the female. The pharynx measures 0·056 to 0·059 mm.×0·099 to 0·112 mm. in the male and 0·05 to 0·064 mm. × 0·038 to 0·095 mm. in the female. The œsophageal bulb is composed of two swellings. The anterior one is smaller, elongated

and 0·181 to 0·227 mm. long in the male and 0·2 to 0·225 mm. in the female. The posterior swelling is broader than long and measures 0·254 to 0·272 mm. × 0·290 to 0·363 mm. in the male and 0·272 to 0·275 mm. × 0·291 to 0·3 mm. in the female. The bulb is separated from the remaining portion of the œsophagus by a constriction. The two swellings are also clearly marked on account of a slight neck between them. The posterior swelling contains a valvular apparatus.

The cervical papillæ are small and are situated at a distance of 1·15 to 1·23 mm. in the male and 1·06 to 1·07 mm. in the female from the anterior end. The excretory pore is situated behind the cervical papillæ at a distance of 1·46 to 1·48 mm. in the male and 1·55 to 1·65 mm. in the female, from the same end. The distance of the nerve-ring from the anterior extremity is 0·336 to 0·4 mm. in the male and 0·34 to 0·45 mm. in the female.
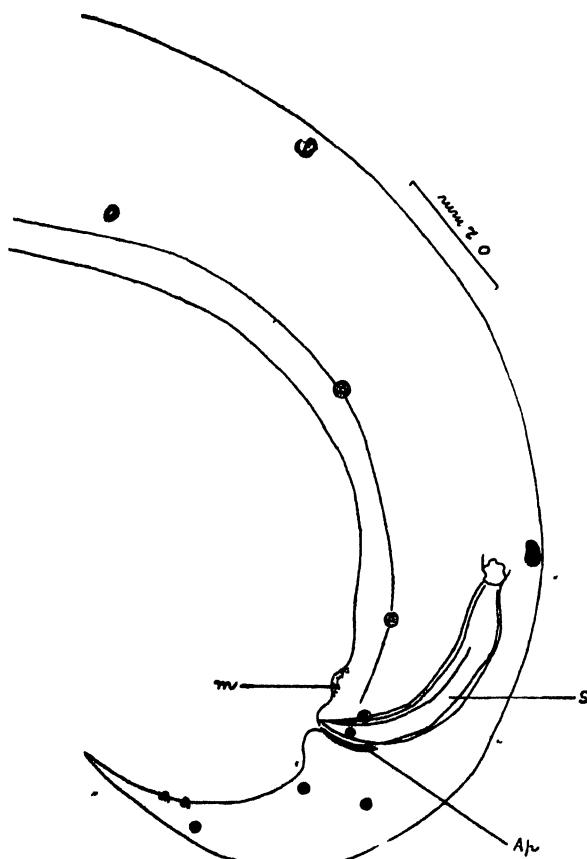
FIG. 2

Spironoura khadrai : Caudal end of male ; lateral view. *Ap.,* accessory piece ; *m.,* median papilla ; *s.,* spicule.

The tail of the male is 0˙36 to 0˙365 mm. long. There are 10 pairs of rather small caudal papillæ and a preanal median papilla. Out of these 10 caudal pairs, 5 are preanal and 5 postanal. Counting from the posterior end, the first and the second are close together and subventral in position ; the third, slightly in front of the second, is subdorsal ; the fourth is subventral ; the fifth, slightly anterior to the fourth, is lateral ; the sixth and the seventh are close and subventral ; the eighth, the ninth and the tenth are situated at a considerable distance from one another. The large median papilla is situated a little anterior to the seventh pair. In a lateral view of the caudal end, the sixth pair appears to be paracloacal but on examining it from the ventral side it is seen to be distinctly preanal.

There is no sucker-like organ. The obliquely transverse and parallel muscle-bands are well developed. The equal and similar spicules are 0˙35 to 0˙38 mm. long. A well-chitinised accessory piece, measuring 0˙085 to 0˙1 mm., is present.
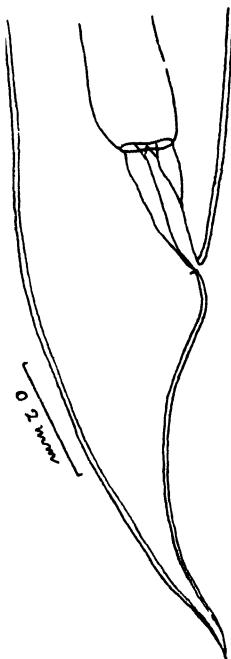
FIG 3

Spiŗonoura khadrai: Caudal end of female ; lateral view.

The tail of the female measures 0˙46 to 0˙61 mm. and is drawn out into a fine point. A pair of caudal papillæ is situated at a distance of

0·19 to 0·32 mm. from the tip of the tail. A little behind this pair, there is an additional pair of inconspicuous papillæ.

The vulva is situated at a distance of 7·5 to 7·6 mm. from the anterior extremity. The lips of the vulva are not developed. The muscular vagina, 0·25 to 0·28 mm. long, runs anteriorly and to the dorsal side for some distance and then joins the two opposed uterine branches. The thick-shelled eggs measure 0·089 to 0·099 mm. × 0·065 to 0·072 mm.

The arrangement of the caudal papillæ in the male of the species described here, is similar to that in *S. duyagi* Tubangui and Villaamil, 1933. But the chief character which distinguishes the latter is the presence of two or three sucker-like organs in the male.

Of the Indian species of the genus Spironoura, the species described above bears a resemblance to *S. falcata* (v. Linstow, 1906). However, the total length of the œsophagus, position of the cervical papillæ and the excretory pore, the length of the tail in the two sexes and the nature of the accessory piece are some of the points in which the two forms differ. It bears even a closer resemblance to the Ceylonese species *S. brevispiculata* Baylis, 1935, as regards some of the measurements. But here also there are some important points of difference between the two. The tooth-like processes on the lips are absent in the Ceylonese species. Also the length of the entire œsophagus is less in it. The positions of the cervical papillæ and the excretory pore are different. The spicules are longer and the caudal papillæ differently arranged in the male of the species under description. Also there are two pairs of caudal papillæ in the female. Finally the length and the form of the tail of the male in *S. brevispiculata* are different, there being a stout terminal spike on the tail, measuring 0·13 to 0·15 mm. long.

It is, therefore, proposed to separate this species from *S. falcata* and *S. brevispiculata* and to name it *S. khadrai*.

Habitat : Intestine.

Host : *Barbus dobsoni*.

Locality : Poona.

Family QUIMPERIIDÆ Baylis, 1930

It appears that the first record of the representative of the family Quimperiidæ was made by v. Linstow (1878) who briefly described

Nematoxys tenerrimus. Stewart (1914) described another Nematode under the name *Heterakis macronis.* As shown below both these species were referred to their proper positions by Baylis. Later Gendre (1926) described *Quimperia lanceolata.* But in his paper he did not give the systematic position of the genus Quimperia created by him. Subsequently (1928), however, he erected a new sub-family Quimperiinæ to accommodate Quimperia and placed it in the family Heterakidæ. Four years later Baylis (1930) described *Gendria tilapiæ* and created a new family Quimperiidæ to replace Gendre's sub-family and to include the two genera Quimperia and Gendria. Another genus Paraquimperia was referred to this family by Baylis in 1934. In attempting to determine some Nematodes from the intestine of an eel (*Anguilla anguilla*) he found that the specimens closely resembled the species *Nematoxys tenerrimus* described by v. Linstow in 1878. Most of the species of Nematoxys have now been referred to other genera and the genus itself is shown to be synonymous with Cosmocerca Diesing, 1861. The exact position of *N. tenerrimus* was, as yet, undecided. Baylis assigned it to the genus Paraquimperia and also amended the diagnosis of the family Quimperiidæ. Yet another genus was recently added by the same author (Baylis, 1939) to this family. While determining the position of *H. macronis* of Stewart, it did not seem possible for him either to retain it in the genus Heterakis or to assign it to any of the existing genera of Quimperiidæ. A new genus Paragendria was, therefore, created to include *H. macronis.*

The family Quimperiidæ now includes the following four genera : —

Quimperia Gendre, 1926. (Type sp.—*Q. lanceolata*).

Gendria Baylis, 1930. (Type sp.—*G. tilapiæ*).

Paraquimperia Baylis, 1934. (Type sp.—*P. tenerrima*).

· Paragendria Baylis, 1939. (Type sp.—*P. macronis*).

Gendria brevispiculum n. sp.

One male and one female of this species were obtained from the intestine of a freshwater fish. The male is 6·95 mm. and the female 5·9 mm. long. The maximum thickness in the male as well as the female is 0·19 mm. and 0·21 mm. respectively. The body of the male as well as the female tapers towards both ends. The caudal end of the male

is curved ventrally. The cuticle has fine transverse striations and is inflated at the anterior end to form a sort of swelling. Cervical alæ
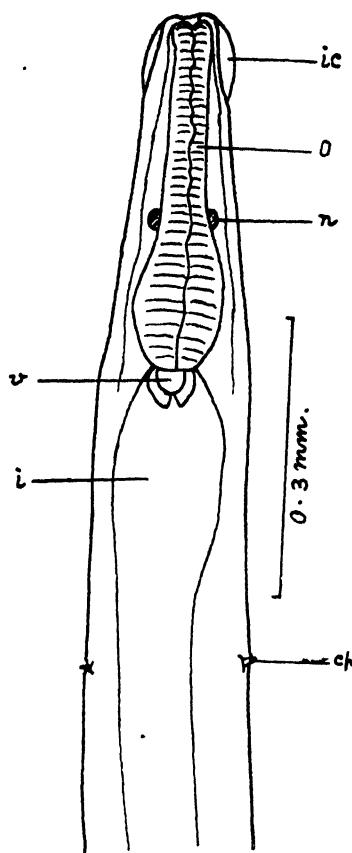
FIG.4
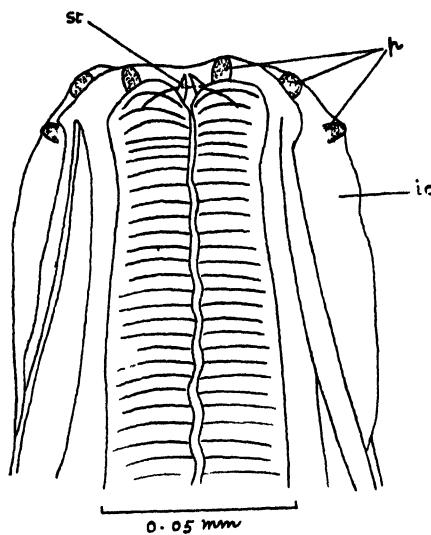
FIG 5

Gendria brevispiculum: Anterior end of male ; dorsal view. *cp.*, cervical papilla ; *i.*, intestine ; *ic.*, inflated cuticle ; *n.*, nerve-ring ; *o.*, œsophagus ; *v.*, valves.

Gendria brevispiculum · Anterior end of male ; higher magnification ; dorsal view. *ic*, inflated cuticle ; *p.*, papillæ ; *st.*, subventral tooth.

are absent. The mouth is a shallow depression and at its base are three conical teeth, projecting from the anterior end of the œsophagus. These are almost of equal size. There are three pairs of cephalic papillæ. The œsophagus is muscular throughout and measures 0·33 mm. in the male and 0·41 mm. in the female. It is club-shaped posteriorly but its anterior end, though a little wider than the preceding part, is not distinctly club-shaped or sub-globular. The intestine is

broad at its junction with the œsophagus and contains three large valves projecting into it. The distance of the nerve-ring from the anterior end is about 0·2 mm. in the male and 0·25 mm. in the female. The cervical papillæ are very small and are situated at 0·65 mm. in the male and 0·61 mm. in the female from the anterior extremity. The excretory pore is situated at about the level of the cervical papillæ.

The tail of the male appears to be about 0·22 mm. long. Unfortunately the tip of the tail is broken in the single specimen at my disposal. Caudal alæ were not observed. There are 15 pairs of caudal papillæ, seven of which are postanal and the remaining preanal. Of the seven postanal pairs four are subventral and three lateral. The papillæ
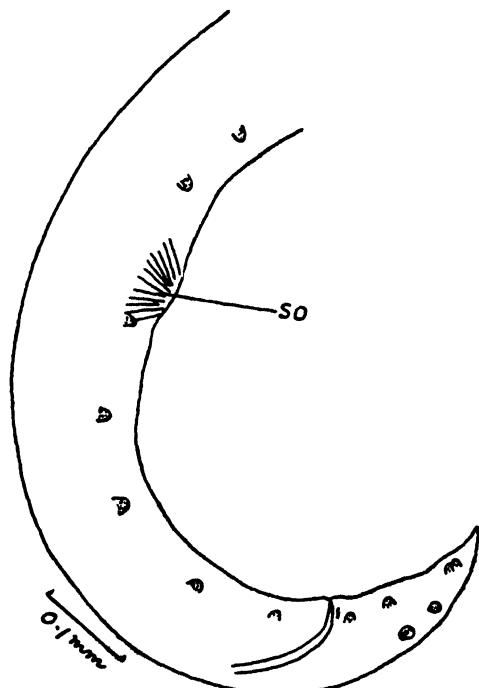
FIG. 6

Gendria breviapiculum : Caudal end of male ; lateral view. *so.,* sucker-like organ.
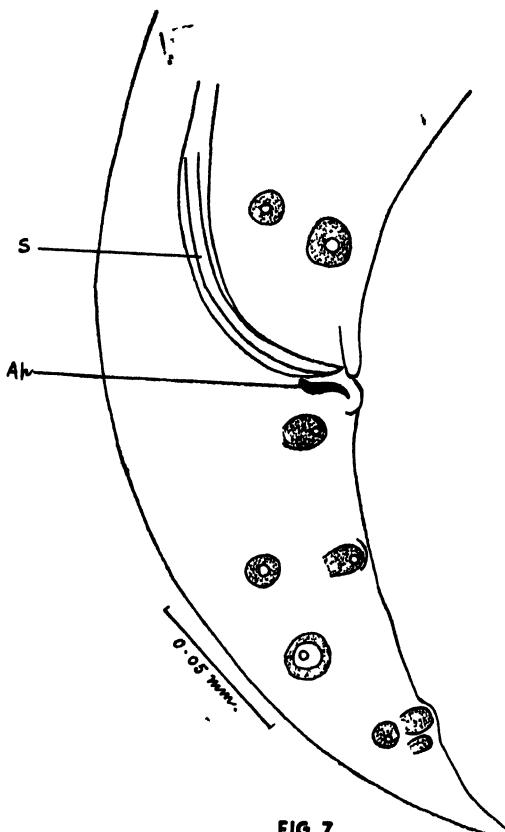
FIG. 7

Gendria brevispiculum : Tail end of male highly magnified ; lateral view. *Ap.,* accessory piece ; *s* , spicule.

forming these postanal pairs are large except those of the first (counting from the posterior end) subventral pair. The second lateral pair is formed by papillæ which are perhaps the largest. The preanal papillæ are comparatively smaller. Of the eight preanal pairs six are situated between the cloacal opening and the sucker-like organ while the remaining two are in front of the latter structure. All the preanal pairs are subventral except one which is lateral. The sucker-like organ is situated at about 0·57 mm. in front of the cloacal opening. The equal, sickle-shaped spicules measure 0·17 mm. and contain a central tubular shaft. A small chitinised accessory piece is present.

The caudal end of the female is straight. The tail is 0·24 mm. long and its tip is slightly rounded. There is a pair of papillæ at 0·15 mm. from the posterior end. The vulva is a transverse slit with undeveloped lips. It is situated at a distance of 2·2 mm. from the tail end. The short muscular vagina runs forward and joins the two directly opposed uterine branches. Fully formed ova were not observed either in the uterine branches or in the vaginal portion.

G. tilapiæ is the only species so far assigned to the genus Gendria. The points of difference between the species described here and the genotype are : (*i*) There are 15 pairs of caudal papillæ in the male.   In the genotype there are 12 pairs.   (*ii*) Caudal alæ are absent in the male ; very slight ones are present in the genotype.   (*iii*) The spicules are much smaller and measure only $0 \cdot 17$ mm., those in the genotype measuring $0 \cdot 41$ to $0 \cdot 49$ mm.

Habitat : Intestine.

Host : Fish (*Macrones* sp.).

Locality : Poona.

Paraquimperia anguillæ n. sp.

The worms, when alive, were slightly reddish in colour.   After fixation, the anterior part in both sexes, curved dorsally.   The posterior end of the male bent ventrally while in the female it remained straight.   The male measures $5 \cdot 43$ to $7 \cdot 2$ mm. in length and $0 \cdot 12$ to $0 \cdot 168$ mm. in maximum thickness.   The female is $9 \cdot 60$ to $12 \cdot 14$ mm. long with a maximum thickness of $0 \cdot 2$ to $0 \cdot 25$ mm.   The lateral alæ, present in both sexes, run throughout the major portion of the body and in the cervical region become wide.   The shallow mouth is surrounded by three
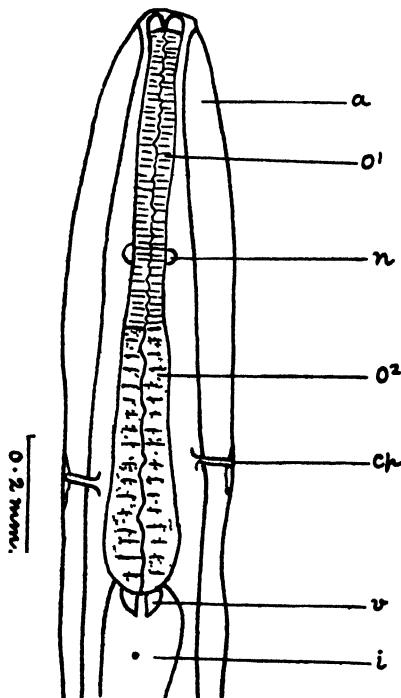

FIG. 8

Paraquimperia anguillæ : Anterior end of female ; dorsal view. *a*., lateral ala ; *cp*., cervical papilla ; *i*., intestine ; *n*., nerve-ring ; *o*¹., anterior part of the œsophagus ; *o²*., posterior part of the œsophagus ; *v*., valves.

small lips, each of which appears to bear a single papilla. In addition there are two pairs of cephalic papillæ. At the base of the mouth there are three sharp forwardly directed teeth situated on the anterior end of the pharynx, which is muscular and 0˙03 to 0˙036 mm. long in the male and 0˙044 to 0˙046 mm. in the female. The œsophagus is composed of two parts, an anterior muscular and a posterior glandular. The first
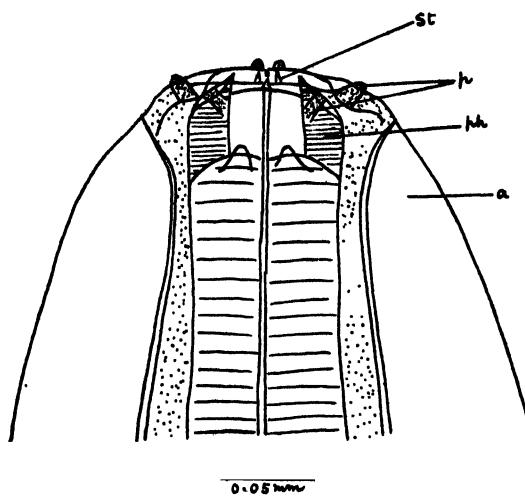
FIG. 9

Paraquimperia anguillæ : Anterior end of female, under higher magnification; dorsal view. *a*, lateral ala ; *p.*, papillæ; *ph.*, pharynx ; *st.*, subventral tooth.

part of the œsophagus is tubular, comparatively long and 0˙3 to 0˙314 mm. in the male and 0˙56 to 0˙633 mm. in the female. The glandular œsophagus, measuring 0˙275 to 0˙28 mm. in the male and 0˙5 to 0˙577 mm. in the female, is wider than the first part and is club-shaped posteriorly. The œsophagus opens into the intestine through an aperture guarded by valves. The slender cervical papillæ cross the lateral alæ at a distance of 0˙45 to 0˙591 mm. in the male and at 0˙833 to 0˙922 mm. in the female from the anterior end. The nerve-ring encircles the first part of the œsophagus in its posterior half and is at a distance of 0˙26 mm. in the male and 0˙366 to 0˙5 mm. in the female from the same end. The excretory pore is at about the same level with the nerve-ring or a little behind it.

The non-alate tail of the male measures 0·27 to 0·3 mm. and
ends in a point. Immediately behind the cloacal opening, the diameter
of the body suddenly diminishes. In the preanal part well developed
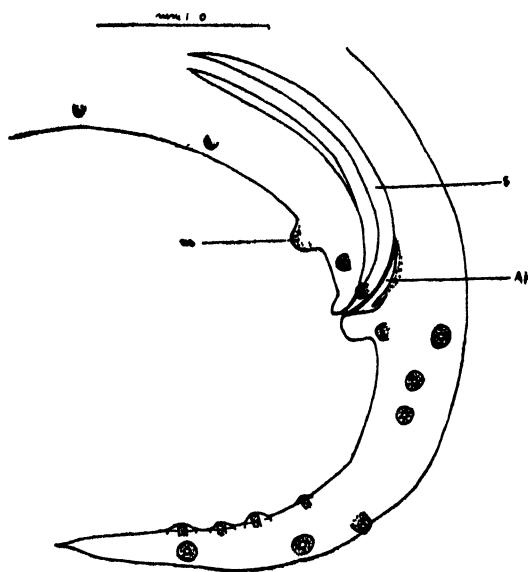
FIG. 10

Paraquimperia anguillæ : Caudal end of male ; lateral view. *Ap.*, accessory piece ;
m., median papilla ; *s.*, spicule.

oblique and parallel muscle-bands are present. There is no preanal
sucker. The sickle-shaped spicules are equal and measure 0·22 to 0·26
mm. in length. There are 15 pairs of caudal papillæ and a large
preanal median papilla. Of the 15 pairs, 11 are postanal and 4 preanal.
All the preanal pairs are subventral, but the fourth one (counting from the
anterior end) situated just anterior to the upper lip of the cloacal opening,
is inclined to be somewhat lateral. Of the postanal pairs, three are
subdorsal, three lateral and five subventral. Their arrangement is shown
in the figure. An accessory piece is present.

The tail of the female ends in a fine point and is 0·38 to 0·435 mm.
long. It bears a pair of small papillæ at 0·22 to 0·23 mm. from the
posterior end. The vulva is situated in the posterior third of the body
and its distance from the tip of the tail is 2·79 to 3·81 mm. The
lips of the vulva are well developed and consequently the vulvar slit appears
to be situated on a conical projection. In some specimens the upper
lip is more developed and almost covers the lower one. Immediately
behind the vulva the diameter of the body is considerably reduced. The
muscular vagina runs anteriorwards for some distance and joins the two
narrow and directly opposed uterine branches. The eggs measure 0·068
to 0·072 mm. × 0·046 to 0·054 mm.

The chief characteristics which distinguish the present form from *P. tenerrima* is the large number of the caudal papillæ and their arrangement and the small size of the spicules.

Habitat : Intestine.

Host : *Anguilla bengalensis.*

Locality : Poona and Nagpur.

<div align="center">GENUS METAQUIMPERIA NOV.</div>

<div align="center">*Metaquimperia callichroi* n. sp.</div>

Worms belonging to this species were collected on two occasions from the small intes ine of *Callichrous bimaculatus.* One lot contained two males and one female and the other a few males and females. The body is straight in the females while that of the male is curved ventrally at the caudal end. The male measures 14 95 to 16·6 mm. and the female 14·8 to 17·15 mm. Their maximum thickness is 0·18 to 0·22 mm.
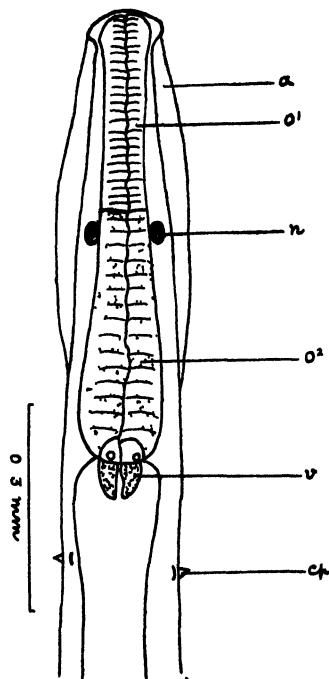
FIG. II

Metaquimperia callichroi.—Anterior end of female, dorsal view a , lateral ala , cp., cervical papilla ; n., nerve-ring , o¹ , anterior portion of the oesophagus ; o², posterior portion of the oesophagus , v., valves.

and 0·21 to 0·23 mm. respectively. The cuticle appears to be smooth. Wide lateral alæ start from the head, become still wider

in the cervical region, attaining the maximum breadth of 0·04 to 0·05 mm. in the male and 0·035 to 0·04 mm. in the female, gradually diminish in breadth beyond the nerve-ring and apparently end at the level of the excretory pore or a little beyond the cervical papillæ in the males. In the females these alæ generally end in front of the posterior end of the œsophagus, but they may extend a little beyond it.

0·05 mm.
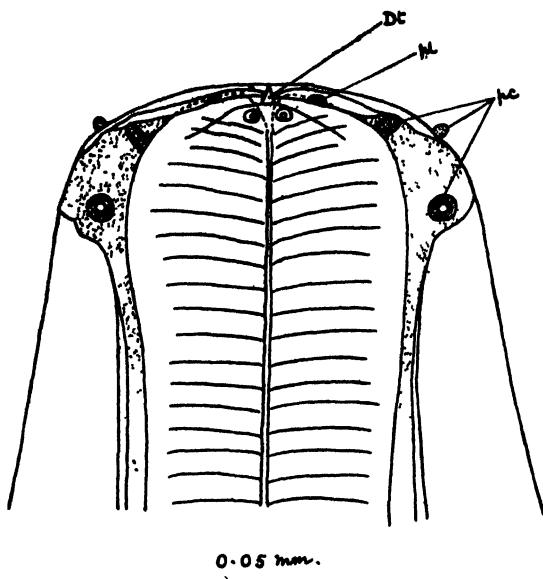
FIG 12

Metaquimperia callichroi.—Anterior end of female, highly magnified, dorsal view
Dt., dorsal tooth ; *pc.*, cocephalic papillæ ; *pl.*, papilla on the lip.

The anterior end is somewhat flattened antero-posteriorly. The mouth is bounded by three somewhat flat and broad lips, each bearing two papillæ. There are at least three pairs of cephalic papillæ present. Situated at the anterior end of the œsophagus are three, one dorsal and two subventral, forwardly directed teeth. The œsophagus is 0·52 to 0·70 mm. long in the male and 0·59 to 0·65 mm. in the female. It is composed of two parts, an anterior muscular and a posterior muscular-granular. The first division of the œsophagus is subglobular at its front end and continues almost up to the level of the nerve-ring where the second part begins. The muscular-granular part gradually widens posteriorly, is distinctly club-shaped and opens in the intestine through a valvular apparatus. The first part of the œsophagus is a little shorter than the second. At its junction with the œsophagus the intestine is broad but its diameter diminishes posteriorwards. The nerve-ring surrounds the œsophagus at 0·27 to 0·36 mm. in the male and at 0·31 to 0·32 mm. in the female from the anterior end. The cervical papillæ are small and their distance from the front end is 0·84 to 0·86 mm. in the male and 0·77 to 0·78 mm. in the female. The excretory pore

is very small and is situated either at the level of the cervical papillæ or
a little in front of them.
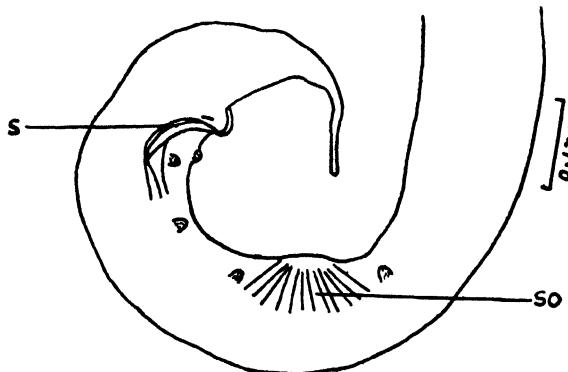
FIG. 13

Metaquimperia callichroi.—Caudal end of male ; lateral view. *s.,* spicule ;
so., sucker-like organ.

The caudal end of the male is bent ventrally. The tail measures $0^{.}24$
to $0^{.}34$ mm. The parallel transverse muscle-bands are well developed.
In the preanal region some of these converge to form a sucker-like
organ which is situated about $0^{.}31$ to $0^{.}42$ mm. in front of the cloacal
opening. There are four pairs of preanal papillæ, one of which is in
front of the sucker-like organ and the remaining three between it and
the cloacal aperture. One pair is paracloacal in position. There is a pair
of small papillæ situated on the anterior margin of the cloacal opening
and a large one on the posterior margin. There are six pairs of postanal
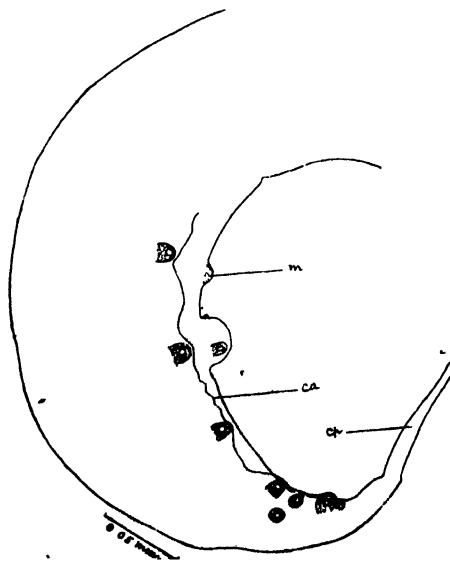
FIG. 14

Metaquimperia callichroi.—Caudal end of male under higher magnification ; lateral
view. *ca.,* caudal ala ; *cp.,* caudal spike ; *m.,* median papilla.

papillæ, five being subventral and one lateral. Two of the subventral pairs are smaller. In addition, there is a large median papilla in front of the cloacal aperture. The specicules are equal and measure 0·17 to
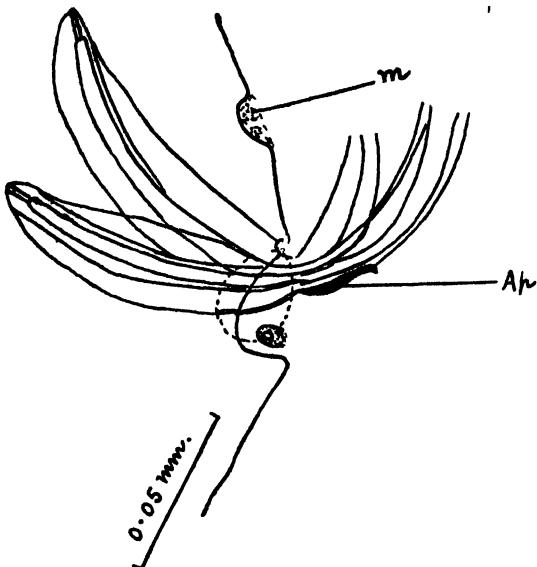
FIG. 15

Metaqnimperia callichroi —Spicules and the accessory piece, lateral view. *Ap*, accessory piece, *m*, median papilla

0·19 mm. They are winged and contain a chitinised central tubular shaft, the terminal portion of which is smaller in diameter and appears to be separated from the main body of the shaft. The lips of the cloacal opening are prominent. There is a small fully chitinised accessory piece measuring about 0·025 mm. in length.

The tail of the female is straight and 0·38 to 0·41 mm. long. It gradually tapers behind and bears a pair of papillæ. The vulva is situated in the posterior half of the body at a distance of 5·1 to 6·7 mm. from the caudal tip. The body of the female appears somewhat constricted in the region of the vulva. The muscular vagina runs forwards and dorsalwards and at about 0·2 mm. from the vulva, meets the two directly opposed uterine branches. There is an ovejector at the beginning of the vagina measuring 0·05×0·04 mm. The eggs measure 0·045

to 0·055 mm.×0·035 to 0·04 mm. The shell of the egg is thin and is slightly thickened internally at the two poles. The contents of the eggs are unsegmented.

This species cannot be assigned to the genera Gendria and Paragendria because their characters are so different. To certain extent it resembles the genus Paraquimperia. It, however, differs from it in the presence of a preanal sucker-like organ. It shows a close resemblance to *Quimperia lanceolata* which is the genotype of Quimperia. Though there is a close resemblance, the differences are equally important. The lips in the present form are broad and flattened while they are semiglobular in *Q. lanceolata*. The œsophageal teeth at the base ot the lips are not present in the latter species. The œsophagus of the form described here is club-shaped both anteriorly and posteriorly and is divided into muscular and muscular-granular parts. The genotype of Quimperia does not show these characters. The length and the structure of the spicules in the two species is considerably different. The number of the caudal papillæ in the male is smaller and the accessory piece absent in *Q. lanceolata*. It does not appear, therefore, possible to assign the form described here to the genus Quimperia. A new genus, with the following characters, is, therefore, erected to include it :

Metaquimperia, gen. nov.—Mouth bounded by three small lips A dorsal and two subventral teeth present at its base. Oesophagus club-shaped anteriorly and posteriorly ; composed of an anterior muscular and a posterior muscular-granular portion. Wide lateral cervical alæ present. Preanal sucker present. An accessory piece present in the male. Spicules alate.

Genotype : *Metaquimperia callichroi.*

Habitat : Intestine.

Host : *Callichrous bimaculatus.*

Locality : Poona. ,

Metaquimperia bagarii n. sp.

Several specimens of this parasite were found in the intestine of a Siluroid fish. The anterior ends of the males and females

curved dorsally and the caudal ends of the males curved ventralwards after fixation.
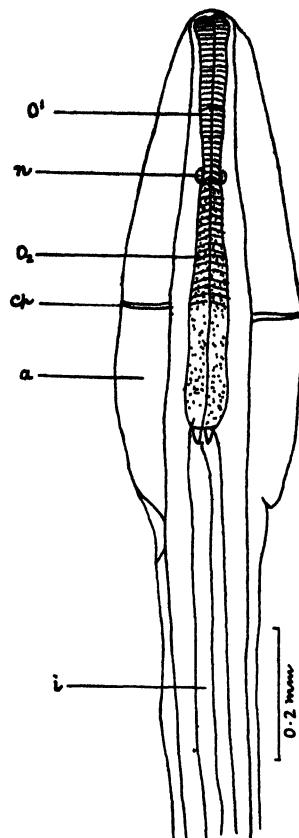
FIG. 16

Metaquimperia bagarii : Anterior end of female ; ventral view. *a.*, lateral ala ; *cp.*, cervical papilla ; *i.*, intestine ; *n.*, nerve-ring ; O^1., anterior part of the œsophagus ; O^2., posterior part of the œsophagus.

The male measures 6·4 to 7 mm. and the female 6·7 to 7·05 mm. The maximum breadth of the body is at the level of the posterior end of the œsophagus or a little behind it and measures 0·13 to 0·15 mm. in the male and 0·15 mm. in the fe.nale. Fine longitudinal striations are present on the cuticle. Lateral alæ are present in both sexes. These start from the head, rapidly increase in width to attain a maximum of 0·06 to 0·09 mm. in the male and 0·09 to 0·1 mm. in the female, either at the level of the cervical papillæ or a little behind them, and run posteriorwards to end in front of the anal opening. From the point of maximum width the alæ begin to decrease gradually, but behind the posterior end of the œsophagus their breadth suddenly diminishes and for the rest of their length they run as very narrow membranes. On account of the greater width of these alæ in the

cervical region and their sudden diminution behind the œsophagus, the front end of the worm has an appearance resembling the head of a spear.
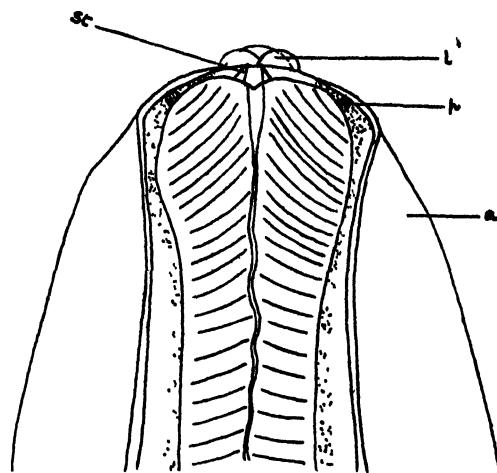
0·05 mm.

FIG 17

Metaquimperia bagarii: Anterior end of female under higher magnification ; ventral view. *a.*, lateral ala ; *l.*, protruded lip ; *p.*, papilla ; *st.*, subventral tooth.
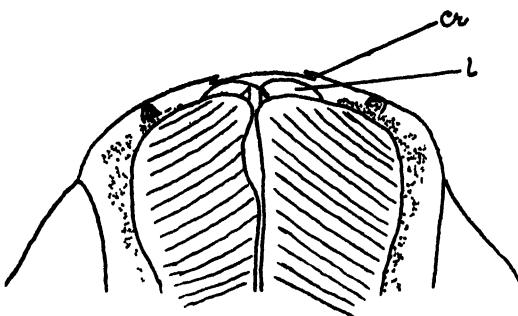
0·05 mm.

FIG. 18

Metaquimperia bagarii : Anterior end of male ; ventral view. *cr.*, cuticular ring ; *l.*, retracted lip.

The rounded head is slightly wider than the portion just preceding it. The mouth is surrounded by three small lips, one dorsal and two subventral. There is a cuticular ring, formed by slight thickening of the cuticle, at the anterior end through which the lips can be protruded or withdrawn. No papillæ were observed on the lips. A single pair of

somewhat laterally placed cephalic papillæ is present. The œsophagus
is muscular throughout and measures 0·61 to 0·66 mm. in the male
and 0·62 to 0·8 mm. in the female. Two parts can clearly be
observed in the œsophagus. The first part is only muscular and its
diameter gradually diminishes from front behind. It is 0·22 to 0·26
mm. long in the male and 0·23 to 0·25 mm. in the female, and
is club-shaped anteriorly. There are three small teeth, one dorsal and
two subventral, at the base of the lips projecting from the œsophagus.
The second part of the œsophagus is muscular and granular and begins
about the level of the nerve-ring. It is a club-shaped structure measuring
0·39 to 0·4 mm. in the male and 0·38 to 0·41 mm. in the female.
In all the specimens the first half of this second division is muscular-
granular, while the remaining portion appears feebly muscular and more
granular. This second part of the œsophagus gradually widens from
front behind. The œsophagus opens through a valvular apparatus into
the intestine which is a narrow tube of uniform diameter. The nerve-
ring is situated at 0·25 to 0·27 mm. in the male and 0·26 to 0·32
mm. in the female from the anterior end. The cervical papillæ
are slender and run across the lateral cervical alæ at a distance of 0·3 to
0·45 mm. in the male and 0·41 to 0·5 mm. in the female from the same
end. The excretory pore was not observed.
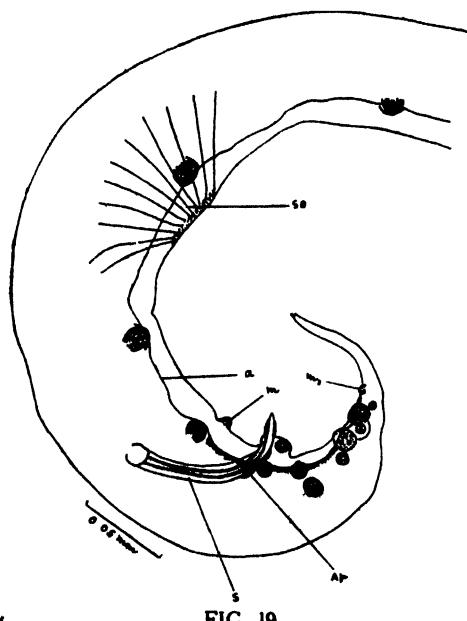
FIG 19

Metasuimperia bagarii : Caudal end of male ; lateral view. *a.,* caudal ala ; *Ap.,* accessory piece ;
m₁, m₂, median papillæ ; *s.,* spicule ; *so.,* sucker-like organ.

The caudal portion of the male is thick and in some individuals forms a loose coil. The tail measures 0·16 to 0·19 mm. and posteriorly has a stout spike which terminates in a small spine. Caudal alæ are fairly well developed. A large preanal sucker-like organ without cuticular rim is present. There are 13 pairs of caudal papillæ, four of which are preanal, one adanal and eight postanal. There are two median papillæ, one in front of the cloacal opening and the other situated at the base of the caudal spike. Counting from the posterior end, the first pair is lateral
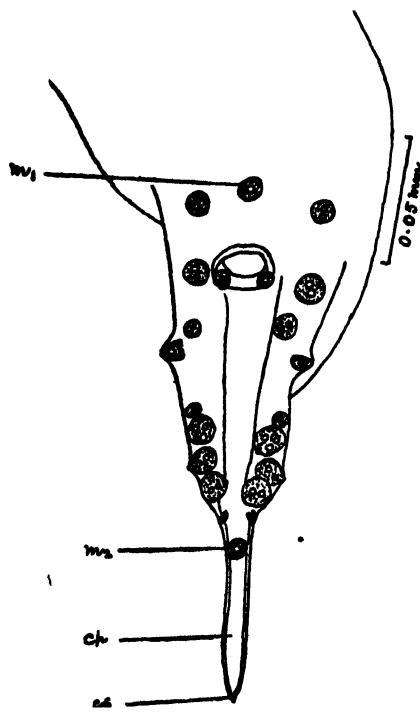
FIG. 20

Metaquimperia bagarii : Caudal end of male ; ventral view. *cp.,* caudal spike ; *cs.,* small caudal spine ; m_1, m_2, median papillæ.

and small. The papillæ forming the second pair are large and subventral. The third pair is small, lateral and a little anterior to the second pair. The fourth pair resembles the second in size and position. The fifth is small and lateral. The sixth is the largest of the lateral pairs. The seventh is subventral. The eighth is ventral and is situated on the posterior margin

of the cloacal opening. The ninth is adanal. All the four pairs of
preanal papillæ are subventral.
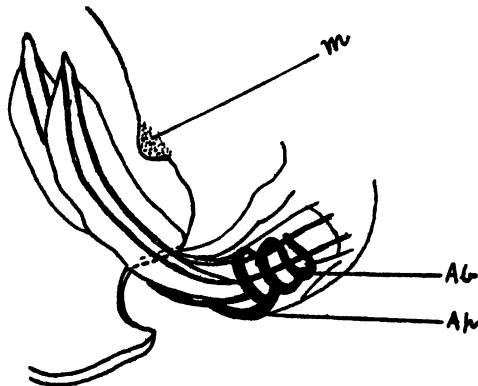
FIG. 21

Metaquimperia bagarii : Spicules and accessory piece ; lateral view. *Ab.,* coiled cuticular band
attached to the accessory piece ; *Ap.,* accessory piece ; *m.,* median papilla.

The spicules are sickle-shaped, equal and 0˙08 to 0˙095 mm. long.
They contain a chitinised central tubular shaft and possess broad alæ.
These, however, do not reach their tips. A chitinised accessory piece is
present. Attached to the proximal end of the accessory piece, there is
a chitinised band which appears to wind round the spicules like the coils
of a screw.
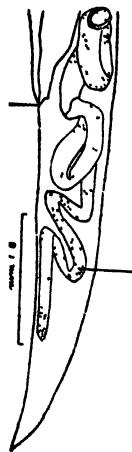
FIG. 22

Metaquimperia bagarii : Caudal end of female ; lateral view. *an.,* anus ; *ov.,* ovary.

The tail of the female is tapering and is 0˙24 to 0˙27 mm. long.
It ends in a small spine. There is a pair of small papillæ just in front
of the tip of the tail. The vulva is in front of the posterior third of the
body and is situated at 2˙5 to 2˙55 mm. from the posterior end. The

upper lip of the vulva is more developed. The vagina is muscular and short. It runs dorsally anterioiwaids and at about 0·1 mm. from the vulva joins the two directly opposed uterine branches. The eggs measure 0·045 × ·035 mm. and their contents are unsegmented.

This species differs from *Metaquimperia callichroi* in having semiglobular lips, a comparatively slender œsophagus, two median papillæ in the male, smaller spicules and an accessory piece with a coiled chitinised band attached to it.

Habitat : Intestine and rectum.
Host : *Bagarius yarrelli*.
Locality : Poona.

<p style="text-align:center">Family : SPIRURIDÆ Orley, 1885</p>

<p style="text-align:center">*Heliconema ahiri* n. sp.</p>

The male of this species measures 21·45 to 25·1 mm. in length and 0·475 to 0·6 mm. in maximum thickness. The female is 27·3 to 32·72 mm. long with a maximum thickness of 0·55 to 0·95 mm. The posterior portion of the male is spirally coiled having two or three turns. The cuticle appears to be inflated in the cervical as well as the cephalic region and forms a cuticular collar round the lips. Posteriorly, this inflated cuticle extends up to the level of the cervical papillæ. There are fine cross striations on the cuticle.
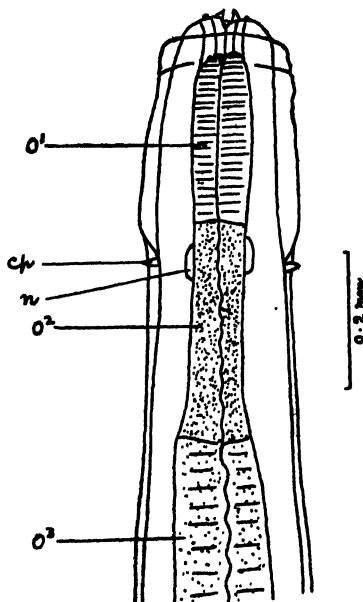
<p style="text-align:center">FIG. 23</p>

Heliconema ahiri : Anterior end of female ; dorsal view. *cp.*, cervical papilla ; *n.*, nerve-ring ; O^1., first part of the œsophagus ; O^2., second part of the œsophagus ; O^3., third part of the œsophagus.

There are two large lateral lips each of which bears a conical tooth on its inner side and three papillæ. The oral cavity measures 0·05 to 0·06 mm. The œsophagus is divided into three parts. The anterior portion is muscular and is 0·22 to 0·265 mm. long in the male and 0·24 to 0·25 mm. in the female. The second portion is granular in appearance and measures 0·24 to 0·29 mm in the male and 0·29 to 0·33 mm. in the female. The third portion of the œsophagus appears muscular and granular, is considerably longer and opens into the intestine by a valvular apparatus. Its length in the male is 4·0 to 4·3 mm. and in the female 4·3 to 4·65 mm. The nerve-ring encircles the second part of the œsophagus near its front end and is at a distance of 0·35 to 0·36 mm in the male and 0·36 to 0·44 mm. in the female, from the anterior end. In both sexes, the somewhat
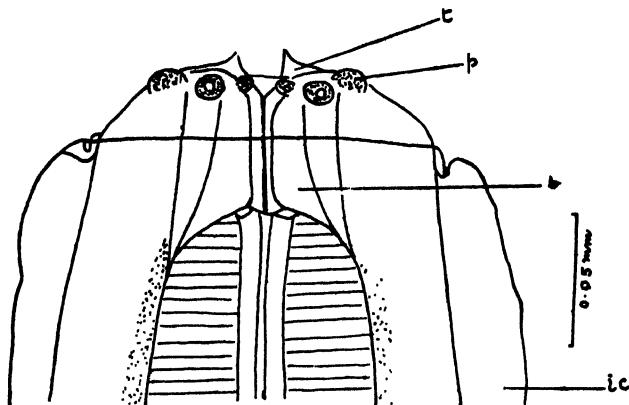
FIG. 24

Heliconema ahiri : Anterior end of female under higher magnification ; dorsal view. *b.,* oral cavity ; *ic.,* inflated cuticle ; *p.,* papilla ; *t.,* tooth on the lip.
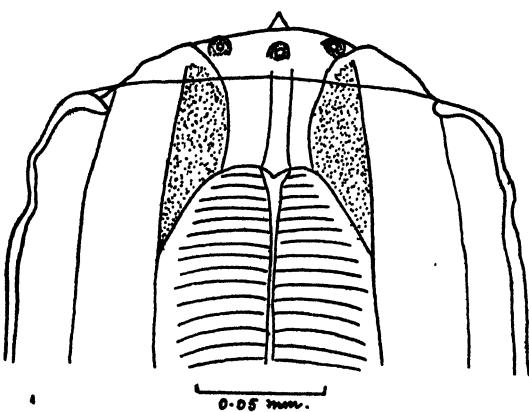
FIG. 25

Heliconema ahiri : Anterior end of female under higher power ; lateral view.

prominent cervical papillæ are either situated in a level with the nerve-ring or a little in front or behind it. The distance between them and the anterior extremity is 0˙35 to 0˙38 mm. in the male and 0˙36 to 0˙42 mm. in the female. The small excretory pore is situated in the neighbourhood of the anterior end of the muscular-granular œsophagus and is at 0˙47 to 0˙58 mm. in the male and 0˙53 to 0˙58 mm. in the female from the anterior end.

Though the posterior part of the male is coiled, it does not possess an asymmetrical ala, but is tessellated on the ventral side, in front of the cloacal opening. Caudal alæ are well developed. There are eleven pairs of pedunculate caudal papillæ. Four of these are preanal and the

0˙2 mm.
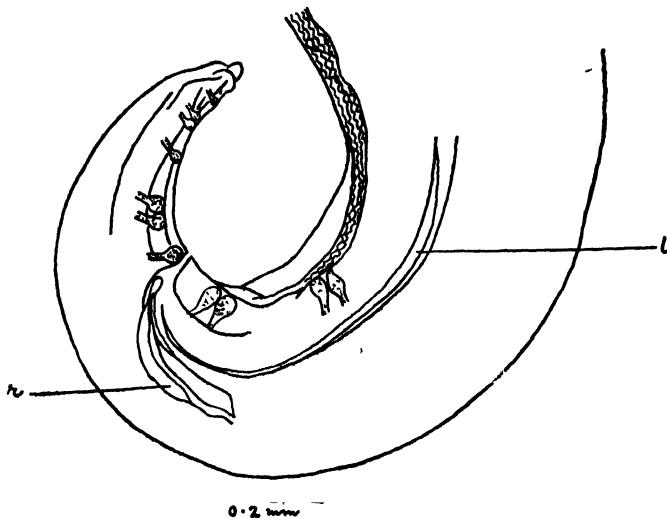
FIG. 26

Heliconema ahiri : Caudal end of male ; lateral view.   *l.,* left spicule ; *r.,* right spicule.

rest are postanal. Beginning from the posterior end, at about 0˙07 mm. there is a single pair ; in front of this there are two pairs together ; in front of this group there is another single pair. About 0˙13 mm. anterior to this pair there are again two pairs of large papillæ situated together. Immediately behind the cloacal opening is a single pair of large papillæ. The preanal papillæ are all large and are arranged in two groups of two pairs each, one in front of the anal aperture and the other at some distance anteriorwards from this. The tail of the male is 0˙36 to 0˙46 mm. long and ends in a rounded tip. The spicules are unequal and dissimilar. The right one is small, broad and boat-shaped. It tapers distally and has a blunt rounded end. It is 0˙25 to

0·27 mm. long.   The left spicule is alate in the anterior two-thirds of its length and measures 0·63 to 0·77 mm.

0·1 mmw.
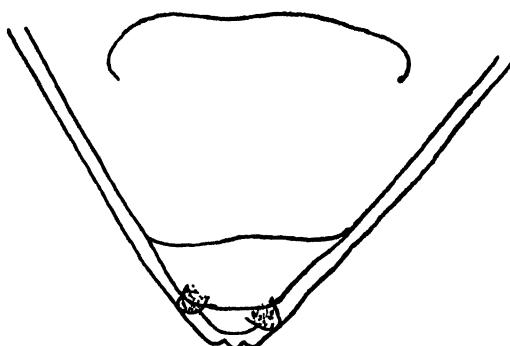
FIG. 27

Heliconema ahiri : Tail of female ; ventral view

The tail of the female is conical and 0·12 to 0·13 mm. long.   It is truncate and bears a very small cuticular spine.   At about 0·02 mm. from the posterior end there is a pair of papillæ.   The vulvar opening is roughly triangular and is situated at 14·15 to 15·62 mm from the anterior end.   It has feebly developed lips and leads into a small roundish ovejector which is surrounded by unicellular glands.   The muscular vagina runs backwards to a distance of about 0·25 mm from the vulva and then turns forwards.   After reaching a point about 0·22 mm. in front of the vulva it again turns back and about 0·47 mm. behind the vulva joins the two opposed uterine branches.   The thick-shelled eggs measure 0·035 to 0·045 mm. ✕ 0·025 to 0·03 mm.

As far as the writer is aware of, the following three species of Heliconema are known up to present : *H. heliconema, H. brevispiculum* and *H. anguillæ.* The present form resembles *H. anguillæ* described by Yamaguti (1935), but may be distinguished from it by the presence of 11 pairs of caudal papillæ in the male :—

> Habitat : Stomach.
> Host : *Anguilla bengalensis.*
> Locality : Poona.

Family CAMALLANIDÆ Railliet and Henry, 1915

Camallanus ophicephali Pearse, 1934

Dr. Bhalerao's collection contains nine tubes of Nematodes   obtained from fishes.   One of them contains this species recovered from the stomach of *Ophiocephalus marulius.*   The locality of the host is not mentioned on the label.

Unfortunately the material consists of a single mature female. It is remarkable in not possessing the tridents associated with the buccal apparatus.

The female measures 12·6 mm. in length and 0·22 mm. in maximum thickness. The cuticular cross striations are very fine.' The dorsoventral diameter of the head measured at its anterior angles is 0·085 mm. The
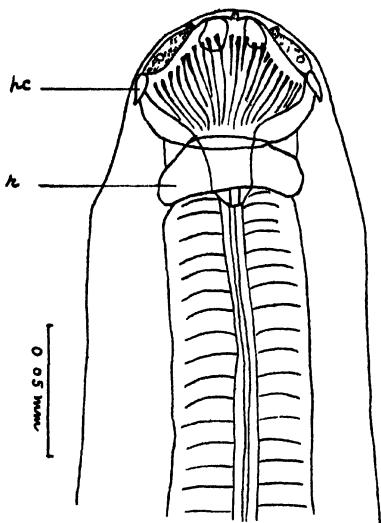
FIG 28

FIG. 29

Camallanus ophiocephali : Anterior end of female, lateral view   *pc*, cuticular projection in place of the trident ; *r.*, posterior ring of the buccal apparatus.
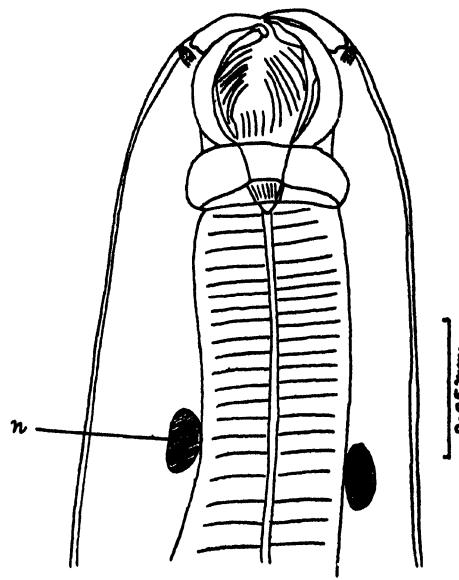
Camallanus ophiocephali : Anterior end of female ; dorsal view. *n*, nerve-ring.

chitinised buccal valves are broader than long and measure 0·05 × 0·08 mm. There are 23 internal longitudinal ridges on each buccal valve and on the outer side there are two irregularly oval thickenings of the cuticle. The posterior ring is heavily chitinised and somewhat curved posteriorwards. Its diameter is 0·063 mm. and is about 0·02 mm. thick. The "tridents" are absent but at the place where these structures are usually attached, there are two small chitinised projections. The anterior portion of the œsophagus is muscular and is 0·21 mm. long. The second muscular-glandular portion is considerably longer than the first and measures 0·76 mm. Œsophageal glands, opening in the mouth, appear to surround the greater portion of the œsophagus.

The nerve-ring encircles the muscular œsophagus at a distance of 0·17 mm. from the anterior end. The cervical papillæ are inconspicuous and are situated at 0·2 mm. from the front end. The excretory pore is a little in front of the junction of the first and the second œsophagus and its distance from the anterior end is 0·23 mm.

The tail is finger-shaped and its tip is bluntly rounded. It is 0·27 mm. long and bears a pair of small papillæ in front of the tip. The vulva is situated in front of the middle of the body at a distance o. 6·9 mm.
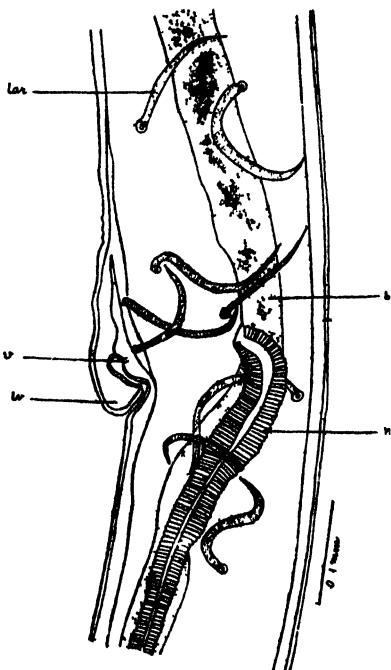
FIG 30

Camallanus ophiocephali . Vulvar region, lateral view ı , intestine , *lar*, larva , *lv* , upper lip of vulva , *mv* , muscular vagina , *v* vulva

from the posterior end. Its upper lip is well developed and overlaps the lower one. The muscular vagina is narrow and runs backwards. At about 0·55 mm. it joins the two opposed uterine branches. The blind end of the posterior uterine tube is situated at 0·44 mm. from the tip of the tail.

This worm resembles the females of *Camallanus ophiocephali* in almost all points and there is no doubt that both are identical. *C. ophiocephali* Pearse, 1934, is rather inadequately described. As the material at my disposal does not contain any male specimens, it would not be out of place to record here the important characters of the male as given by Pearse (1934). The largest male is 4·7 mm. in length and 0·5 mm. in diameter. ' In the male small tridents extend to the posterior margin of the jaws, but such structures are not apparent in the females.' ' The tail of the male 0·09, acute tapering, curved ventrally. There are 4 pairs of postanal papillæ and a pair of discoidal elevations near the tip of the 2 pairs of papillæ are situated immediately in front of the anus and

six pairs some distance in front of these. Right spicule 0·35, left spicule 0·13, cross ridges occur throughout the curved, ventral posterior region of the male.'

Habitat : Stomach.

Host : *Ophiocephalus marulius.*

Procamallanus mehrii Agarwal, 1930

Two males of this species, associated with a large number of larvæ of *Anisakis* sp., obtained from the intestine of *Wallago attu*, were contained in a tube from Dr. Bhalerao's collection. The locality of the host is not mentioned on the label.

The two males are smaller than those described by Agarwal (1930), but they agree very closely with his description of the male. In view of the fact that these worms are from the same host, it would be reasonable to assume that they belong to the same species.

Baylis (1939), in giving the description of this species, remarks, " there are said to be eleven pairs of caudal papillæ, and an unpaired papilla near the tip of the tail, but the arrangement of the papillæ is not clearly described or figured."

In view of the above remarks, it seems desirable to give a redescription of the males of this species based on the material at my disposal.
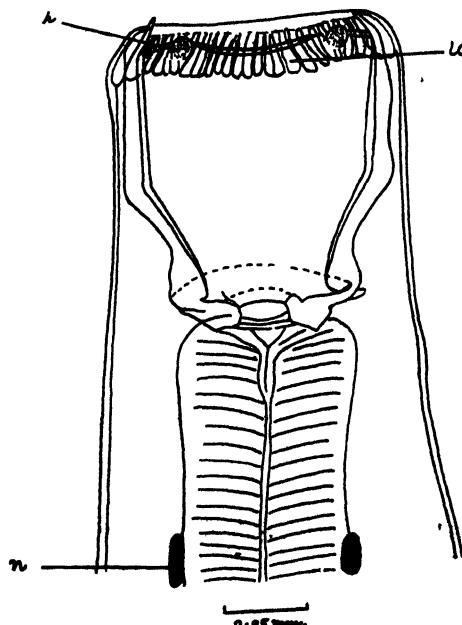
FIG. 31

Procamallanus mehrii : Anterior end of male ; dorsal view.
lc , leaf-crown ; *n.*, nerve-ring ; *p.*, papilla.
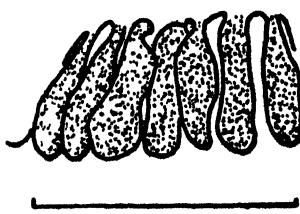
FIG. 31 A

Procamallanus mehrii : ' Leaves ' from the ' leaf-crown '.

The males measure 11·8 to 14·5 mm. in total length and have a maximum thickness of 0·4 to 0·45 mm. The cross cuticular striations are about 0·0025 mm. apart. The buccal capsule measures 0·15 to 0·2 mm. in length and 0·12 to 0·14 mm. in breadth. It is cup-shaped but the anterior end does not appear to be slanting as shown in the figure by Agarwal. There are strips of cuticular thickening on the capsule around the mouth. These are thin at the ends and are in contact with the adjoining ones. The ' leaf-crown,' as seen in an end on view, forms an unbroken ring completely surrounding the mouth. The ' leaves ' are broad posteriorly and taper anteriorly. They have a granular appearance and probably are of the nature of unicellular glands which open in the mouth. There are at least two pairs of papillæ round the mouth. The muscular œsophagus is 0·9 to 0·93 mm. and the muscular-glandular 0·69 to 0·84 mm. in length. The nerve-ring is situated at 0·26 to 0·28 mm. and the cervical papillæ at 0·35 to 0·44 mm. from the anterior end. The excretory pore is at about 0·48 mm. from the same end.
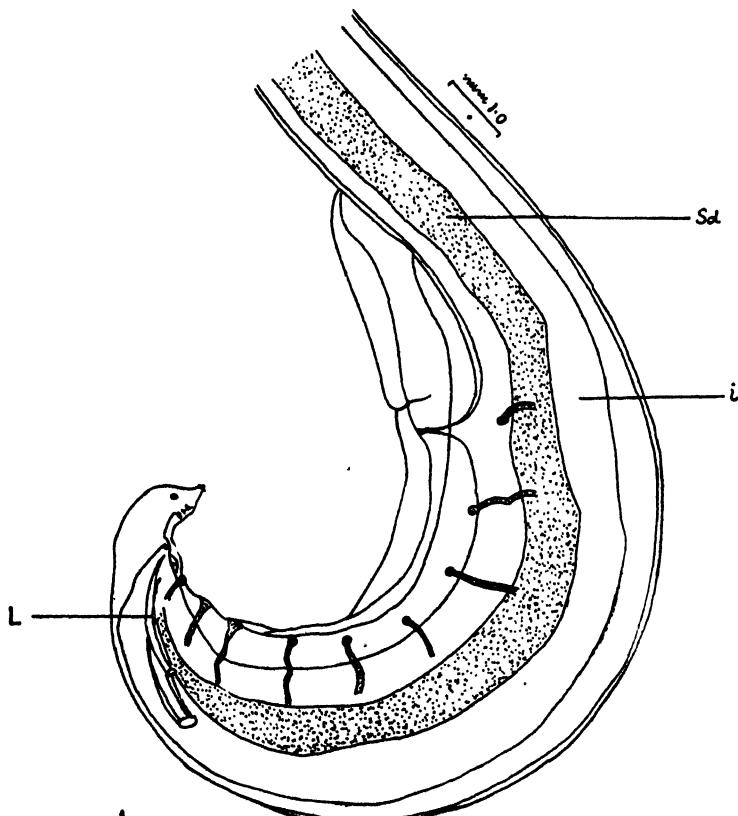
FIG. 32

Procamallanus mehrii : Caudal end of male ; lateral view.
i., intestine ; *L.*, left spicule ; *Sd.*, sperm-duct.

The posterior end of the male is highly muscular and curved ventrally. The tail measures 0·13 mm. Caudal alæ are well developed. There are 18 pairs of caudal papillæ in the males at the writer's disposal. Of these, nine are preanal and are formed of papillæ having long and slender peduncles. The two lips of the cloacal opening bear a single pair
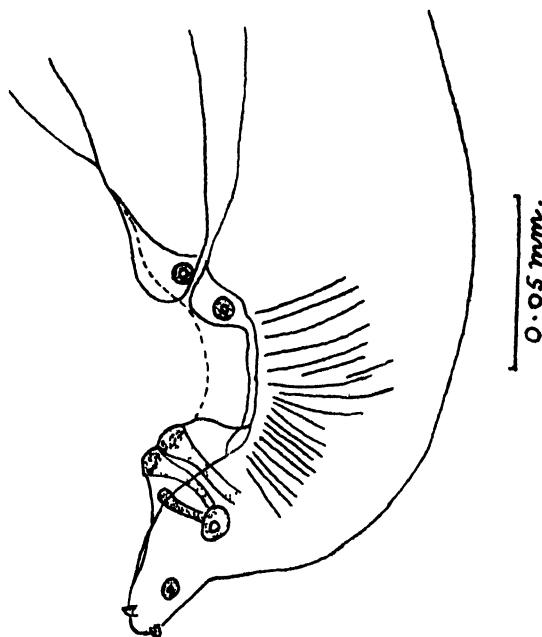
FIG. 33

Procamallanus mehrii   Tail of male highly magnified , lateral view

of papillæ, each. Of the seven pairs of postanal papillæ four are subventral, one subdorsal and the remaining two are lateral. Counting from the posterior end the first pair is subventral and very small. The second pair is subdorsal and in a line with the first pair. The third pair is lateral but shifted a little towards the dorsal side. The remaining four pairs are situated together and form a group. The papillæ of the fourth pair are stalked. The fifth pair is lateral and situated at the base of the fourth and the sixth. The sixth and the seventh are large and their papillæ have long peduncles. The two chitinised spicules are unequal. The right spicule measures 0·25 to' 0·265 mm. in length and its proximal end is broad and truncate. The left is comparatively slender and is 0·19 mm. to 0·21 mm. long. Both spicules end in fine points. There is no accessory piece.

Habitat : Intestine.

Host : *Wallago attu.*

Procamallanus sp.

Dr. Bhalerao's collection contains a single immature female, obtained from the stomach of *Saccobranchus fossilis*, which is referred to the genus Procamallanus.

Paracamallanus ophiocephali n. sp.

The same collection contains a few females obtained from the intestine of *Ophiocephalus gachua*. The locality of the host is not mentioned.

The females are 9·6 to 11·55 mm. long and their maximum thickness is 0·3 to 0·34 mm. Transverse cuticular striations are fine. The head is squarish in shape and its dorsoventral diameter measured at the anterior angles is 0·16 to 0·18 mm. It is followed by a narrower neck. The usual paired chitinised valves are present but in addition there is a chitinous buccal cavity or " pharynx " posteriorly situated. The buccal valves including the pharynx, measure 0·14 to 0·16 mm. Their breadth is about the same. The number of the internal longitudinal ridges on each valve varies between 9 and 11. The ridges near the median line are short and their length gradually increases
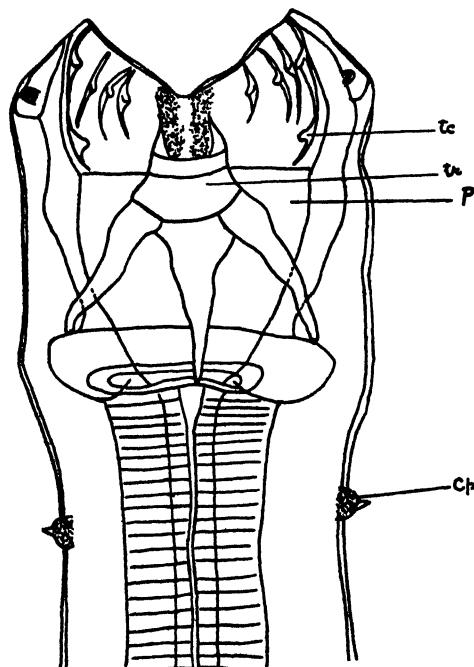
FIG. 34

Paracamallanus ophiocephali ; Anterior end of female ; dorsal view. *P.*, pharynx ; *tc.*, tubercle on the ridge ; *tr.*, trident.

laterally. The ridges bear chitinous tubercles projecting from their surface. These in a lateral view appear as beads on them. Generally there are two to three such tubercles on the longer ridges and a single, situated in the middle, on the shorter ones. The chitinous wall of the buccal cavity shows five internal thickenings, appearing like blunt projections, some of which appear to be connected with the longitudinal ridges situated opposite them. Externally each valve bears a pair of quadrilateral areas of cuticular thickening near their anterior margin. The posterior ring of the buccal apparatus measures 0·1 to 0·13 mm. in diameter and appears to have its rims somewhat upturned. The tridents are well developed, their arms reaching the posterior ring. The lateral prongs are somewhat shorter than the middle one which is about 0·105 mm. long. There are three pairs of papillæ on the head.

The muscular œsophagus measures 0·4 to 0·45 mm. and the muscular-glandular 0·78 to 0·95 mm. in length. The nerve-ring is at a distance of 0·27 mm. from the anterior extremity. The cervical papillæ are conspicuous and are situated in front of the nerve-ring. Their distance from the front end is about 0·24 mm. The excretory pore is situated at the level of the nerve-ring or just behind it.

The tail measures 0·095 to 0·11 mm. and is finger-shaped. Its tip is rounded and blunt. There appears to be a single pair of papillæ immediately in front of the tip of the tail. The vulva is situated in front of the middle of the body. In the largest specimen (measuring 11·55 mm.) it is situated at a distance of 6·6 mm. from the posterior end. The lips of the vulva are not prominent. The vagina is muscular and narrow and measures 0·55 mm. in length. It runs in the posterior direction and dorsal and then turns a little anteriorwards. At a distance of about 0·46 mm. behind the vulva it joins the opposed uterine branches. The anterior ovary reaches the posterior end of the muscular œsophagus. The uterine branches are packed with larvæ. Male unknown.

The female worms described above bear a resemblance to those described under the name *Camallanus sweeti* by Moorthy (1937). But the latter ones may be distinguished from the former by their small size, the character of the ridges on the buccal valves and the three spines at the tip of the tail.

The present species also resembles *Paracamallanus cyathopharynx* (Baylis, 1923), but it may be distinguished from it, in having tuberculated ridges on the valves and a cuticular ring between the pharynx and the œsophagus.

These worms are, therefore, referred to a new species of the genus Paracamallanus.

Habitat : Intestine.

Host : *Ophiocephalus gachua.*

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ON THE CHROMOSOMES OF AN INDIAN TOAD, *BUFO STOMATICUS* LÜTKEN

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INTRODUCTION

A SPECIES of toad, much smaller than the common Indian toad, *Bufo melanostictus*, is spread all over Gujarat. Unlike the latter species it is strictly nocturnal in habit and hides itself below stones, in deep crevices, in gutters and moraines, and below the bark of trees. It is never seen to come out during day-time and bask in the sun-shine jubilantly or hop about in the rains like the common Indian toad. It also does not hold large congregations in ponds and call out its fellow creatures in a riotous cacophony. This is perhaps the reason why it is locally called, *Patal Deduk*, meaning thereby a toad from the deeps.

A few representative specimens of this species collected here were identified by the Director of the Zoological Survey of India as belonging to the species *Bufo stomaticus* Lütken. Our best thanks are due to him for helping us in this matter. There is no account of this species in Boulenger's (1890) "*Amphibia and Reptilia.*" But a year later the same author [*Boulenger** (1891)] described it as a form quite distinct from *Bufo andersinii*. Annandale (1909, 1918) and Narayan Rao (1918), however, are of the opinion that, "it is doubtful whether the two species are distinct." They further say (*op. cit.*, p. 40), "specimens of toad from India assigned to *Bufo andersonii* are certainly identical with the species from Eastern Bengal named *Bufo stomaticus* by Lütken, whose name has priority." This species according to them is distributed all over the Indo-Gangetic plains, in the Western and Eastern Himalayas, up to an altitude of at least 6,000 ft. in Nepal and occasionally in those parts of Bengal and Bihar that lie South of the Ganges Valley. According to Boulenger (1890) this species, which as we have seen, he calls *Bufo andersonii*, is found at Muscat in Arabia, also in Agra, Sind and Rajputana, the regions which are not far removed from North Gujarat, the place where the specimens for the present study were collected. It is interesting to note that Malcolm Smith (1929) has described not long ago a species of toad, which he calls *Bufo stuartii*, from Putao plain, N. E. Burma on the Tibetian frontier. According to him, this species is a close ally of *Bufo stomaticus* Lütken.

Pending a detailed description of the spermatogenesis in this species to be published later, we propose to give here an account of the chromosomes of this species. Bufonidæ have served in the past as interesting material not only for the studies on spermatogenesis but also in the investigations on the phenomena of sex-reversal in the Amphibia. Our object in this investigation was mainly to study the chromosomes of this species ; because, we know so little yet about the chromosomes of the Indian Amphibia. The only investigations made in India, so far as the authors are aware, are by Asana and Kharadi (1937) who have described the chromosomes of the common Indian frog, *Rana tigrina*, an Anuran, and by Seshachar (1936, 1937), who has studied them in *Ichthyophis glutinosus*, a Caecilian. The present study gives an account of the chromosomes of another common Indian Anuran, *Bufo stomaticus*.

MATERIAL AND METHODS

The material for the present study was collected from the vicinity of the Gujarat College, Ahmedabad, practically all the year round. The testes of the animals were fixed at night in Bouin, Allen-Bouin, PFA3, Flemming's strong and weak fluids and Champy. All these fixatives gave good results, the fixation lasting for about 24 hours. The material was washed for 24 hours and dehydrated by passing it through gradually increasing grades of alcohol in distilled water. It was left overnight in 90 per cent. alcohol and transferred to absolute alcohol next day where it stood for two hours, the alcohol having been changed three times at an interval of 45 minutes between two successive changes. The material was then, cleared in Cedar wood oil and left in it overnight. It was subsequently rinsed in tolulin and embedded in paraffin. Sections were cut 10–12 micra thick and stained by Heidenhain's Iron Hæmatoxylin method, and differentiated in saturated solution of picric acid. All the drawings were made with the aid of Abbe's camera lucida under oil immersion at the level of the stage, the magnification being 2,000 times approximately. They are reproduced here at the same magnification.

OBSERVATIONS

A. Primary spermatogonium.—Many primary spermatogonia in an active stage of division were observed in the material collected in the middle of March. They were comparatively few in the testes fixed during other parts of the year. The form of a resting spermatogonium is spherical as has been observed in many other Amphibians by the previous authors. Each primary spermatogonium is surrounded by follicular cells (Fig. 3). The nucleus is polymorphic and shows deeply stained dark granules varying in size. At the metaphase two centrosomes can be clearly seen at the two poles of the spindle, while in the equatorial plate 22 chromosomes are seen, 12–14 of which are large, slender and distributed peripherally (Fig. 4). They are all V-shaped but the two arms of V are not equal in length in all the chromosomes. The angle between the two arms of V is also variable. ' The remaining 8–10 chromosomes are small and distributed irregularly in between the larger chromosomes and in the centre of the plate. These also are V- or U-shaped and show a median constriction.

B. Secondary spermatogonia.—After a brief period of rest the primary spermatogonia give rise to secondary spermatogonia which become progressively smaller in size as they undergo repeated cell divisions. The form of the nucleus also changes. It is no longer polymorphic but spherical (Fig. 5). After their last division the secondary spermatogonia get converted into primary spermatocytes. These also are surrounded by follicular cells and lie usually in groups. They possess 22 chromosomes of the same kind as are found in the primary spermatogonia, but these elements are shorter than the corresponding ones in the primary spermatogonia, and they lie closer to one another (Figs. 6 and 7). The large peripheral chromosomes are often clear but the short chromosomes present some difficulty in counting them. But in some good plates 22 chromosomes have been counted (Figs. 6 and 7).

C. Primary spermatocytes.—As has been stated above these are derived from the last division of the secondary spermatogonia. After going through a series of changes characteristic of meiosis, they show the reduced number of chromosomes at the metaphase. It is interesting to note in this connection that in diakinesis there appears an element which is larger than the rest of the bivalents and lies separate from them. Its shape also is different from that of the rest of the bivalents as shown in Fig. 11. The behaviour of this element is similar to that of a V-shaped tetrad observed in the chromosomal complex of *Bufo bufo japonicus* by Minouchi and Iriki (1931). In the polar view of the metaphase there are in all 11 tetrads mostly of the dumb-bell type so common in Salamanders, *Amphiuma* and other Amphibians. Six of them are large and five are small. A typical arrangement of these as seen in equitorial plates is shown in Figs. 8 and 9. In the side view of the spindle at this stage there appears a bivalent the two component elements of which are larger than those of the rest of the bivalents. It lies at the periphery of the spindle more or less vertically and forms a V-shaped tetrad (Fig. 10). Very probably the components of this bivalent represent the sex-chromosomes of the XX type.

D. Secondary spermatocytes.—The metaphase plates of this category of cells showing well separated chromosomes are not frequently met with in the young growing testes. But in the material fixed in the second week of April some plates were found which showed six large and five small, more or less V-shaped chromosomes (Fig. 12).

E. Bidder's organ.—Hermaphroditism is quite common in toads, particularly in the genus *Bufo*. One often comes across the testicular ova in this animal. Many a time the lower-most tubules of a testis give rise to ova (Fig. 1). Sometimes the ovarian follicles develop adjacent to the lower end of a testis and surrounding a short length of the vas deferens as it gets free from the outer border of the testis (Fig. 2). These peculiarities are associated with sex-reversal and allied phenomena found to be common in this genus by previous workers like Ponse (1924), Witschi (1933) and others. In this genus the Bidder's duct persists up to the adult condition of the gonad and forms an ovo-testis as shown in Fig. 2.

What happens to these ova is not known but similar cases showing Bidder's organ in Amphibia have been noted by Ponse (1924), Welti (1928), and Stohler (1926) in *Bufo*, by Swingle (1917), Crew (1921), Rau and Gatenby (1923), in *Rana*, by Moszkowska (1932) in *Bombinator*, by Champy (1921) in *Triton*, and by Seshachar (1939) in *Uraeotyphlus*.

REMARKS

Spermatogonial chromosomes.—The genus *Bufo* has been worked out by several authors and the number of the spermatogonial chromosomes recorded by them is given in the Table below :—

	Species			Spermatogonial chromosomes	Author	Year
1.	*Bufo lentiginosus*	..	..	24	King ..	1902, 1907
2.	*Bufo viridis*	..	..	22	Stohler ..	1926
3.	*Bufo calamina*	..	..	22	Stohler ..	1927
4.	*Bufo vulgaris**	..	..	22	Stohler ..	1928
5.	*Bufo bufo japonicus*	..	..	22	Iriki ..	1929
6.	*Bufo sachalinensis*	.	..	22	Makino ..	1930
7.	*Bufo stomaticus*	.	..	22	Asana and Mahabale ..	1941

*Della Valle (1907) gives 18–24 as the number of oogonial chromosomes in *Bufo vulgaris* (*vide* Oguma and Makino, 1932, *Journ. Genet.*, 26, p. 241).

As will be seen from the Table given above, only one of the previous authors differs from all other recent investigators in her observations on the number of chromosomes found in the species she studied. However, in view of the improved technique employed by the majority of the recent authors, the number 22 is more likely to be the correct number of the spermatogonial chromosomes.

Sex chromosomes.—We have not made any very critical observations on the spermatogonial and the bivalent chromosomes of the primary spermatocytes with a view to determining which of these elements represent the sex chromosomes.   There is much difference of opinion among the previous authors regarding the connection between sex determination and any particular chromosomes in the chromosomal garniture of Amphibia.   And this situation has been well summarised by Iriki (1930).   In this direction we have little to say beyond observing that the element marked " V " in Figs. 10 and 11 as observed in diakinesis and metaphase is most probably the sex chromosome bivalent in this species.

SUMMARY

1. *Bufo stomaticus* Lütken is a species of small toad fairly common all over Gujarat.   It is nocturnal in habits, seeking cover at day-time, hiding in mud, in deep crevices or under the bark of trees.

2. Its spermatogonial chromosomes are 22 in number. 14 of these are large and V-shaped and lie on the periphery of the spindle, while 8, which are also V-shaped but small, occupy the central region of the metaphase plate.

3. These two groups of chromosomes form 11 tetrads in the primary spermatocytes, 6 of which are large and 5 small. All of them are more or less dumb-bell shaped excepting one which assumes the form of a broad V when seen in a side view of the spindle, and lies nearer to the periphery. It can be traced to the stage of diakinesis where it can be made out by its size and position, it being the largest chromosome lying somewhat apart from all other chromosomes.

4. Bidder's organ so common in other species of *Bufo* is found in this species also. It embraces the lower part of the testis and a portion of the vas deferens at the point where the latter becomes free from the testis.

EXPLANATION OF PLATE FIGURES

All the figures shown in Plates I and II have been drawn with the aid of Abbe's camera lucida at the level of the stage under oil immersion using Leitz's No. 17 occular and 2 mm. apochromatic objective. The magnification of the figures in Plate II is 2000 times approximately.

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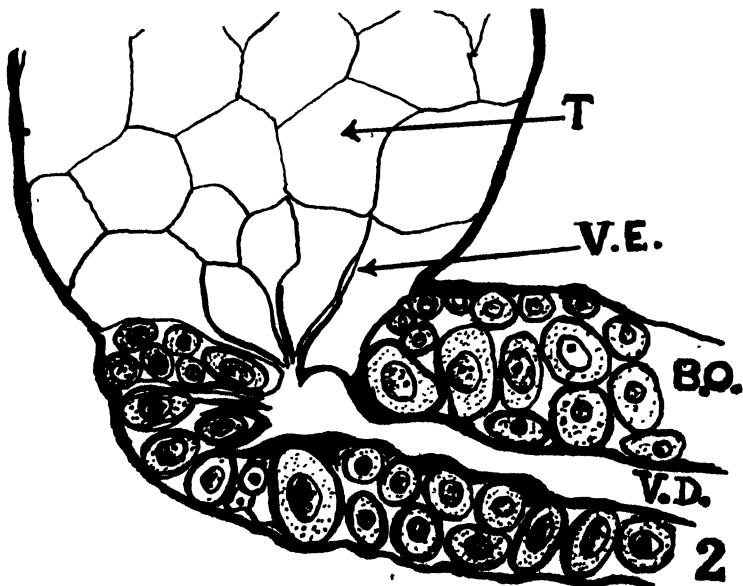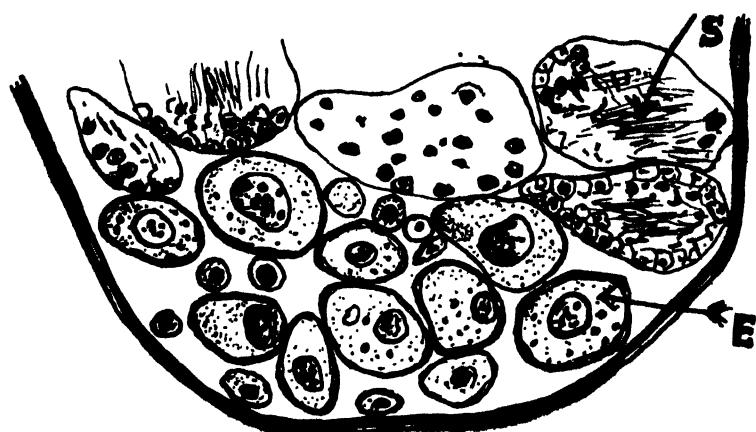
Figs. 1 and 2. *Bufo stomaticus* Lütken. x 50.

Fig. 1. Longitudinal section of a testis showing eggs E in the lowermost loculi and sperms S in the loculi above these.

Fig. 2. Longitudinal section of a testis T with Bidder's organ B. O. at its posterior end, encircling the *vasa differentia* V. D.; V. E.—*vasa efferentia*.
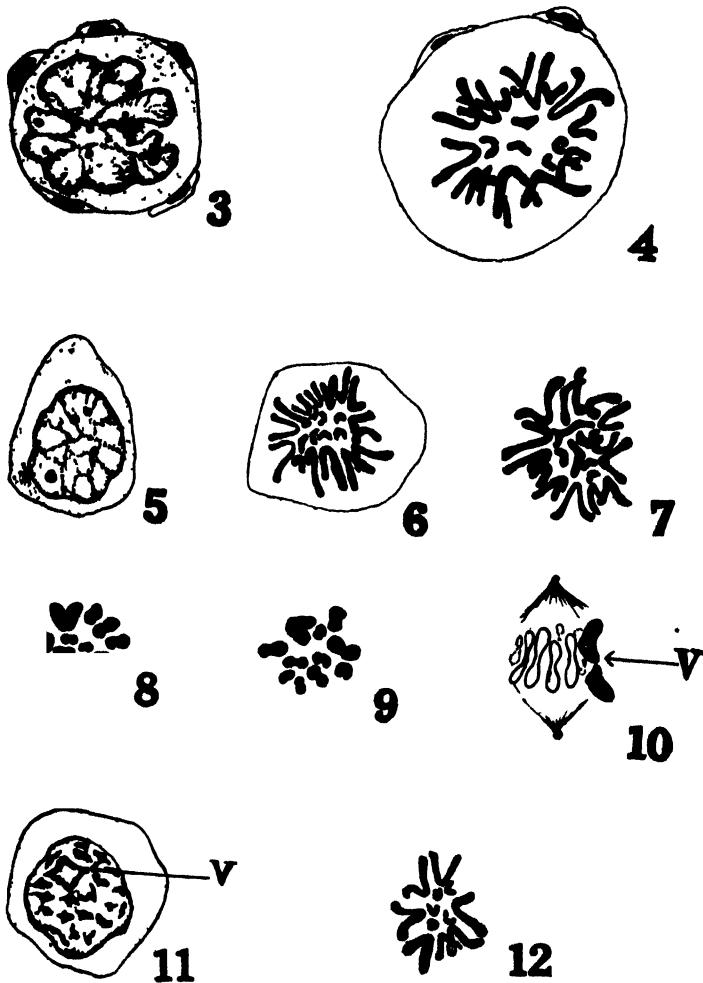
Fig. 3. A primary spermatogonium at rest. Fig. 4. Polar view of the metaphase plate of a primary spermatogonium showing 22 V-shaped chromosomes. Fig. 5. A resting secondary spermatogonial cell. Figs. 6 and 7. Polar view of the metaphase plates of the secondary spermatogonia. Figs. 8 and 9. Equatorial plates of the primary spermatocyte showing 11 bivalents. Fig. 10. Side view of the spindle at the metaphase of a primary spermatocyte showing a vertical V-shaped tetrad marked " V ". Fig. 11 Primary spermatocyte undergoing meiosis : diakinesis. Note the large V-shaped element, marked " V ". Fig. 12. Metaphase plate of the secondary spermatocyte showing 11 univalent chromosomes.

CYTOLOGY OF THE COMMON BOMBAY FIBRE ALOE, *AGAVE VIVIPARA* L.

PART I.—MICROSPOROGENESIS

By

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INTRODUCTION

THE plants belonging to the Agavoideæ are economically important for their fibre yielding character. The leaves and roots produce excellent fibre, generally known as pita or *wakh* (in Marathi), the American aloe fibre or the vegetable silk. The fibre is used for cordage. According to Woodrow (1910, pp. 537–539) seven species[1] of *Agave* are commonly grown in the gardens and fields in India. By far the commonest of all the species cultivated in the Bombay Presidency is *Agave vivipara* L. It is usually cultivated along the banks of canals and borders of fields. Since the species is one of economic importance, it was thought worthwhile to work out its cytology in order to know its genetic constitution.

Literature on the tribe Agavoideæ is fairly extensive and has been thoroughly reviewed very recently by Joshi and Pantulu (1941). References to literature show that the genus *Agave* has been worked out cytologically by Osterhaut (1902), Lary de Latour (1908), Schaffner (1909), Catalano (1929, 1930), McKelvey and Sax (1933), Doughty (1936) and Vignoli (1936). The number of chromosomes in various species of *Agave* so far studied by several authors is given by Joshi and Pantulu (1941). The present paper gives the chromosome number for one more species, namely, *Agave vivipara* L.

MATERIAL AND METHODS

The anthers of *Agave vivipara* were fixed at Poona in the months of May, October and January on clear sunny days between 12 noon and 2 p.m. The fixatives used were : Navaschin's, Carnoy's, Allen's modification of Bouin's fluid and Schaffner's. The slides were prepared by the usual paraffin method, using Iodine Gentian Violet or Heidenhain's Iron-alum Hæmatoxylin as the stains. There was not much difficulty in obtaining stages of the early development of the sporangia, but the stages of reduction division in the pollen-mother cells required a great deal of effort.

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[1] *A. vivipara, A. americana, A. vivipara,* var. *Cookii, A. cantala,* var. *variegata, A. Woodrowi, A. sisalana, A. rupicola.*

OBSERVATIONS

Meiosis.—Fig. 1 shows a sporogenous cell at rest in a young anther. It is polygonal in shape and many such cells are compactly grouped together in a young anther. Two large nucleoli, unequal in size are seen in the nucleus. The cytoplasm shows an alveolar appearance. With the onset of prophase, the cell increases in dimensions and the nucleus enlarges considerably. A single nucleolus is seen at this stage as a dark body surrounded by a hyaline perinucleolar zone, probably an artefact (Fig. 2). The chromatin seems to be distributed more towards the periphery and forms small irregular blocks (Fig. 2). These give rise to leptonema threads which undergo synapsis (Fig. 3). The nucleolus is seen as a dark body at this stage and lies outside the mass of threads. The leptonemal threads are usually lying irregularly, but later on they show some polarization (Fig. 4). The leptonemal threads conjugate parasynaptically. The paired appearance of the thread, however, is soon lost and they collapse into a tight knot characteristic of synizesis (Fig. 5). This stage is now generally regarded as an artefact. Gradually the knot of the chromosomes becomes loose and the bivalents again become distinct. Chiasmata are clearly seen during the diplotene and diakinesis stages (Figs. 6, 7, 9). Two pairs of chromosomes were seen attached to the nucleolus at zygotene and early diakinesis stages (Fig. 8) as was observed by Joshi and Pantulu (1941) in *Polianthes tuberosa.* At diakinesis 30 bivalents can be clearly counted (Fig. 9). Twenty-five of them are small and five large. The nucleolus now begins to lose its staining capacity and becomes a faintly stained body. The nuclear membrane also becomes indistinct and is lost. Fibres in the form of conical hoods appear at the two poles of the nucleus and they form the achromatic figure (Figs. 10 and 12). The spindle enlarges and the chromosomes lie at its equator (Figs. 10 and 11). The configuration of the metaphase plate commonly met with, is shown in Figs. 13 and 14. There are two kinds of chromosomes, 5 large more or less V-shaped and 25 small, which are dot-like and vary in size. The large chromosomes lie at the periphery of the plate and the small ones in the centre. The former sometimes show terminal or interstitial chiasmata. The spindle is of the normal type and the chromosomes in the anaphase also show normal behaviour. Movement of the chromosomes is usually synchronous, but cases showing laggards were not altogether wanting (Figs. 16, 17). The occurrence of chromatid bridges was also noted in one or two cases (Fig. 18). Multipolar spindles were noticed rarely (Fig. 15), as previously observed by Schaffner (1908) in *A. virginica.* These irregularities probably cause irregular distribution of chromosomes and result in the development of bad pollen grains, but their proportion in an anther-lobe is significantly small. Telophase and second meiotic division were found to be normal. During interkinesis the spindles usually lie at right angles to each other but they may be parallel also. The pollen-mother cells divide according to the successive type.

Pollen.—In a ripe anther most of the pollen grains are of a uniform size, but a few showing a size smaller than the usual one were also met

with. Their proportion, however, is approximately less than 10 per cent. The outer surface of the pollen grain is reticulated and bears a few warts also.

Tapetum.—The tapetum is of the secretion type as has been observed by Schnarf (1931). The tapetal cells are small, deep staining, and tabular in a young sporangium (Fig. 19) and enlarged and multinucleate at the time of reduction division (Fig. 20).

GENERAL CONSIDERATIONS

Sterility.—*Agave vivipara* belongs to the sub-genus *Euagave*. Most of the species of this sub-genus are known to reproduce by bulbils and suckers, but they also bear fruit sometimes, and form seeds. Although the proportion of fruits to the bulbils on a panicle is small, the seeds whenever are formed, are properly developed and viable. As the great majority of the pollen grains in this species is formed normally, the reason of the sterility, viviparous habit, and the dearth of seeds in most cases cannot be the bad pollen grains. The true explanation of the sterility must be, therefore, sought along other lines.

Chromosomal complex.—It has been customary to place the genus *Agave* under Amaryllidaceae, but the chromosomal complex of *Agave vivipara* conforms to the *Yucca*-type of Sato (1934) and justifies the separation of the genus *Agave*, along with some other genera, into a separate family, Agavaceae, as proposed by Hutchinson (1934). For further discussion on this point the recent paper by Joshi and Pantulu (1941) may be consulted. There are 30 n chromosomes in this complex. Five chromosomes are large and V-shaped and the rest are small and dot-like.

Genetic constitution of Agave vivipara and its systematic position.— Doughty (1936) has studied many species of *Agave* growing at Amani and has come to the conclusion that 30 appears to be the basic number for the genus *Agave* (n=30). The following species of *Agave* along with *Agave vivipara* studied in the present paper, have 30 n chromosomes : *A.amaniensis, A.Bouchei, A.Sartorii, A.Haseloffii, A.filifera, A.micracantha, A.angustifolia, A.americana, A.consociata* and *A.virginica*. It is now generally believed that *Agave vivipara* is synonymous with *Agave cantala*. According to Doughty (1936) there are 90 chromosomes, 15 large and 75 short, in *Agave cantala* ; and therefore, he considers it to be a triploid species (3 n=90). Since there are 30 chromosomes (n=30) in haploid state and 60 (inferred) in 2n condition in *Agave vivipara*, it is extremely unlikely that *Agave cantala* and *Agave vivipara* are co-specific. Older botanists like Dalzell, Woodrow and others were probably right in considering it to be a distinct species.[1]

SUMMARY

Agave vivipara L. shows 30 n chromosomes of which five are large, V-shaped and twenty-five small and dot-like. Meiotic divisions do not

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[1] A similar opinion about this species has been expressed by the Curator of the Herbarium, Royal Botanic Garden, Calcutta, in a letter to one of us (T. S. M.), dated July 15, 1941.

deviate far, from the normal. Irregularities and bad pollen grains are less than 10 per cent. From its chromosomal complex it appears to be a species quite distinct from *Agave cantala* which according to Doughty (1936) has 90 diploid chromosomes.

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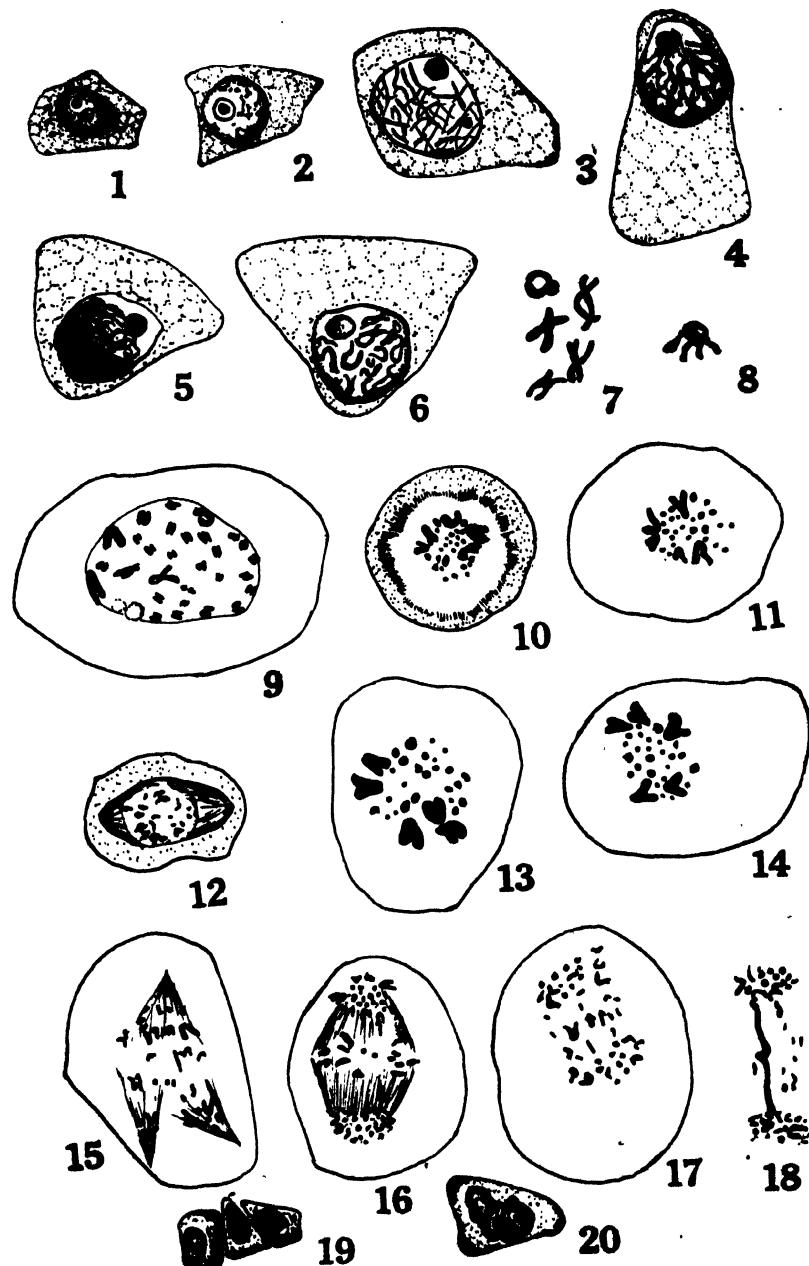
Figs. 1-20. *Agave vivipara* L. Figs. 1-14. Different stages of the first meiotic division in the pollen-mother cells up to metaphase. Figs. 1 and 2. Two pollen-mother cells with resting nuclei. Figs. 3 and 4. Leptotene. Fig. 5. Synizesis. Fig. 6. Diplotene. Fig. 7. Chiasmata at the diplotene and diakinesis. Fig. 8. Two pairs of chromosomes attached to the nucleolus at zygotene. Fig 9. Diakinesis. Figs. 10-12. Three premetaphase stages. Figs. 13 and 14. Polar view of two metaphase plates showing 30 n chromosomes. Figs. 15-18. Irregularities in the meiotic process. Fig. 15. A multipolar spindle. Figs. 16 and 17. Asynchronous movement of the chromosomes. Fig 18. Chromatid bridge. Figs. 19 and 20. Tapetal cells. Fig. 19. Tapetal cells in a young anther. Fig 20. A tapetal cell in an anther at the time of reduction division. Figs. 1-18. X 1200. Figs 19 and 20. X 250.

THE STUDY OF THE FEMALE GAMETOPHYTE AND A TROPHOPHYTE IN *EPHEDRA FOLIATA* BOISS

By

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Introduction

GNETALES is a very fascinating group of Gymnosperms and Hagerup (1934) has recently revived interest in it by claiming it as an intermediate group between Gymnosperms and Angiosperms. The author's interest in this group was aroused by certain interesting observations that he had made and by the abundance of *Ephedra foliata* near Karachi.

It is found at Thatta, which is sixty miles from Karachi towards Hyderabad. It is also found at Bund-Muradkhan which is about seventeen miles north of Karachi ; and it grows abundantly on both sides of the railway lines running from Karachi Cantonment Station to Drigh Road Station.

Maheshwari (1935) finds *Ephedra foliata* as a climber over *Prosopis Specigera, L.* This plant is not found in abundance in the Drigh Road area and we find *Ephedra* associated with *Euphorbia nerifolia, Linn*, and also sometimes with *Capparis aphylla,* Roth.

The flowering time of these plants in Sind invites attention. Cook (1901) says that *Ephedra foliata* flowers in March and April and Mehra (1934) confirms this. Talbot (1911) also found it to be so but mentions that sometimes the plants flower in October. The author has found these plants flowering throughout the year and there is no month in which either the staminate or the pistillate plants have not been seen in buds or in flowers.

Previous Work

The papers available are very few. In 1907 appeared a paper by Berridge, E. M. and Sanday A. on " Oogenesis and Embryogeny in *Ephedra distachya.*" In 1909 Berridge wrote a paper on " Fertilization in *Ephedra altissima.*" In 1913 appeared Land's paper on " Fertilization and Embryogeny in *Epherda trifurca.*" Herzfeld in 1922 gave a description of *Ephedra camphylopoda.* In 1935 Maheshwari contributed to the morphology of the gametophytes of *Ephedra foliata.* In 1940 Rayat Khan wrote a note on double fertilization in *Ephedra foliata.*

Material and Methods

Plenty of material in various stages of development was available throughout the period of the work. I usually fixed the material on the spot in the morning and sometimes also in the afternoons and the evenings.

Chromo-acetic-acid with the addition of half a per cent. maltose was found to be a very satisfactory fixative. In the Laboratory the bracts of the well developed female flowers were removed and the flowers were put in fresh fixatives. Sometimes the bracts were removed and the ovules were cut transversely near the micropylar as well as chalazal ends and sometimes only the female gametophytes were fixed in a very weak solution of the Chromo-acetic-acid. Iron-alum hæmatoxylin was mostly used, sometimes to the stain was added five per cent. acetic acid and this improved the staining immensely.

OBSERVATIONS

The megaspore begins to form the gametophyte very early in the development of the ovule. The nucleus of the megaspore divides and forms two nuclei (Fig. 1). These nuclei move towards the two opposite poles and a vacuole is formed between them. The next stage is the four-nucleate one. In this stage the nuclei are not equidistantly placed from each other (Fig. 2). This free nuclear division continues for a time and I think that in the first few divisions is simultaneous (Fig. 3). In all these stages the cytoplasm and the nuclei are confined to the periphery while the centre is occupied by a large indistinct vacuole. As the free nuclei of the gametophyte are being formed the megaspore first rapidly elongates towards the chalazal end and then towards the micropylar end. When the nuclei are fully formed and the wall formation is about to begin, the gametophyte shows a tendency towards shrinkage as is observed by Maheshwari (1935). Consequently the details of the wall formation are difficult to be made out. I was fortunate to get in a few slides the stages in the wall formation which begins at the periphery of the megaspore and advances towards the centre. Meanwhile the limiting layer of the gametophyte can be distinguished. Then there is a centripetal growth. The innermost cells are open towards the sac cavity. As the centripetal growth proceeds the whole gametophyte increases in bulk, the innermost cells enlarging. When the gametophyte has reached a considerable size the two regions of the gametophyte, namely, the antipodal and the micropylar can be distinguished.

In one or two of my slides I find that the central vacuole is absent and all the space filled with the cytoplasm and the nuclei. Land (1927) finds that careful staining showed the vacuole to be filled at all later stages with a delicate cytoplasmic structure which gradually increases in density. Maheshwari (1935) has also found in some of his preparations cytoplasm and nuclei all over the sac. However, he considers this phenomenon as abnormal and brought about by injuries caused by insects.

The number of the free nuclei in the formation of the endosperm in Gymnosperms before the walls are formed, is very variable. In Ginkgoales (Coulter and Chamberlain 1921), the wall formation begins after the establishment of 256 free nuclei. In *Taxus* it begins after the formation of the same number of nuclei, while in *Pinus* it begins after the formation of 2,000 nuclei.

In *E. trifurca* according to Land (1904) 256 free nuclei are formed before the wall formation begins and all the divisions leading to these nuclei are simultaneous. Berridge and Sanday (1907) state that in *E. distachya* this commences only after 1,000 nuclei have been formed. Maheshwari (1925) could not determine the exact number of nuclei in his preparations but counts the largest number of nuclei to be approximately 500.

My observations show that this nuclear number is not higher in the local specimen than that counted by Maheshwari (1935) for *E. foliata* from the Punjab. Maheshwari (1935) has seen that some of the nuclei lag behind in division and while some nuclei were in metaphase others were in prophase. I am at least inclined to think that the first few divisions are simultaneous in my specimens.

In the centre of the well developed female gametophyte there extends a layer of cells from below the archegonium to the haustorial region. Land (1904) says that in *E. trifurca* these cells are thin walled and richer in food. Maheshwari (1935) also reports similar conditions in *E. foliata*.

In my preparations I do not find any difference in the thickness of the cell walls between the surrounding cells of the female gametophyte and those cells under consideration in the median line. I do not also find any kind of difference in my specimens in the food contents of these cells and the surrounding cells. In my opinion they stand marked out in my specimens from the rest of the cells of the female gametophyte, only because they are elongated in the same direction in which archegonia are elongated. It is along this region that the embryo is pushed down by the elongating suspensor (Fig. 4).

The cells in the gametophyte of Cycadales are uninculeate. Binucleate cells are common in the prothallus of Ginkoales. Sometimes they are also trinucleate and multinucleate. They become uninucleate in the mature gametophyte. Whether this is due to the fusion of nuclei or disorganisation of nuclei, or additional wall formation, remains undetermined (Coulter and Chamberlain, 1921). In the Pinaceæ the gametophyte formation in *Cryptomeria* is peculiar and is described by Lawson (1904). At a time in the developmental stage, hundreds of nuclei divide simultaneously without formation of cell plates. Kinoplasmic fibrils extending between the daughter nuclei increase in number and curve outwards on all the sides until both of the nuclei are completely surrounded by a sheath of fibrils, which fuse to form an investing membrane. Thus a binucleate tissue of endosperm results.

Occasionally in the female gametophyte of the plants studied a kind of division occurs which seems to be similar to that described by Lawson (1904) for *Cryptomeria*. Not that this happens on a big scale but a cell may divide in this manner occasionally. Lawson (1909) finds in *Pseudostuga* free nuclear division occurring in cells of the gametophyte before cross walls appear to form the uninucleate cells of the permanent tissue. In Taxaceæ in some cases the principal growth of the endosperm takes place after fertilization and in other cases before fertilization.

The reason why I am going in such details about the gametophyte formation of the Gymnosperms will be soon clear. Pearson (1929) concludes that the nature of the female prothallium of the genus *Ephedra* is Gymnospermous. He also states that the development of the endosperm in the genera *Gnetum* and *Welwitschia* takes place qn different lines and that this development may be regarded as more advanced than that of *Ephedra*.

The development of female prothallia in Gymnosperms shows lots of variation and no definite conclusions can be drawn from their course as to the remote or more advanced condition of the plants. I am not aware if the female gametophyte of any species of *Ephedra* is studied in detail. According to my observations its course of development runs as follows. The early course up to the wall formation is described earlier. Even when the cell walls are formed and cells are established, the nuclei of certain cells divide. These divisions of the nuclei are not confined to the base or the apex or the middle portion of the gametophyte and are unmistakably by mitosis.

We can divide the whole of the Gametophyte in three parts by drawing two imaginary equidistantly placed transverse lines. In the first division adjacent to the chalazal end the cells are mostly uninucleate. However, there are also occur cells which are binucleate and rarely muntinucleate. These nuclei stain deeply with Iron-Haematoxylin, and they are big and prominent when compared with the nuclei of the micropylar end. These cells are usually square or pentangular (Fig. 5).

The next portion which comes in the centre of the gametophyte is the most interesting. This division contains cell. with granular contents, with well-defined cells walls, and prominent nuclei. These cells are big when compared to the cells of the chalazal end. Usually they are not uninucleate and any number of nuclei may be present in them. Three and four is the most common number, but eight, nine, ten and even twelve nuclei occur in them (Figs. 6, 7, 8, 9 and 10).

Then comes the third portion towards the micropylar end. This part contains cells which are very thin-walled and with less or practically no cell contents. These cells are also either uninucleate, binucleate or multinucleate and are big when compared with the cells of the second division. Their nuclei are not very prominent and not stained well by Iron-Alum-Haematoxylin.

Pearson (1929) has found more nuclei in the cells towards the chalazal end in *Welwitschia*. Compared with *Ephedra*, the latter shows more nuclei in the central part of the gametophyte. This condition of the gametophyte persists up to the time of fertilization.

About the time of fertilization a fusion of nuclei begins to take place all over the gametophyte. In the first division described above, namely towards the chalazal end, the fusion of the nuclei does not seem to be so well marked. However, there is no doubt that nuclear fusion takes

place in this part. The nuclei in the second compartment about the time of fertilization approach each other and begin to fuse. This fusion may involve two, three, four or even up to eight nuclei.

In the third division towards the micropylar end unmistakable fusion also takes place. However, in the fusion of this division few nuclei take part as compared with the nuclear fusion in the central division (Figs. 11, 12, 13, 14 and 15).

This nuclear fusion begins at the periphery in the lower part of the gametophyte and this fusion wave extends inwards and upwards. Even when the nuclear fusion is complete towards the chalazal end the nuclei in the second and third compartments are still fusing. This fusion wave also passes on to jacket cells, the nuclei of which also take part in this fusion wave (P.Ms. 2 and 3).

There is another aspect of the fusion which invites attention. Some of the cells of the female gametophyte, as I have already mentioned, are multinucleate. The nuclei of some of these cells fuse but still they do not form one fusion nucleus. The number of nuclei in these cells varies from one to twelve. Sometimes these nuclei fuse in groups. Not that all of the nuclei take part in this fusion and while some of the nuclei fuse, others remain single. Usually the nuclei fuse in two groups. In some of the cells I have seen three nuclei but one of them was no doubt a result of two or more already fused nuclei.

This can be recognised by the relative sizes of the fusion nuclei. The fusion nucleus resulting from two or more nuclei is comparatively bigger than the original nuclei which enter into fusion.

It must not be supposed however that all the nuclei of the gametophyte fuse. Sometimes some nuclei also fail to fuse and then probably they undergo degenerations.

After the nuclei of the cells of the gametophyte fuse and produce a fusion nucleus, the latter may divide by mitosis, the chromosome number appear to be unusual and abnormal. Darlington (1937) mentions that when polyploid nuclei have arisen they divide by multipolar mitosis, thus resulting in the production of nuclei with chromosome numbers once more reduced. In the nuclei of these cells no multipolar mitosis has been observed. It is quite obvious from what has been said above that the chromosomes counting in the gametophyte cells, just before fertilization, at the time of fertilization or after fertilization is not reliable. However, the counting of the chromosomes in the young gametophyte of *Ephedra* is very easy and dependable.

As a result of the fusion of the nuclei of the female gametophyte there results the development of a true nutritive tissue. Up to the time of the fusion of nuclei no starch is seen in these cells. But after this fusion there begins starch formation. When an embryo is established, there is abundant starch found in these cells, which is useful in nourishing the embryo in the young condition (P. M. 1.).

The embryo sac of *E. foliata* possesses a remarkable degree of plasticity just like that of *Welwitschia*. In *Welwitschia* the nuclear fusion is described as vegetative fertilization by Pearson (1929) which term is equally applicable here.

Thus the morphology of the female prothallus of *E. foliata* becomes very important and interesting.

DISCUSSION

There are difficulties in considering the endosperm of the Angiosperms as homologus with the nutritive tissue resulting from the multiple fusion in *Welwitschia*, *Gnetum*, and *E. foliata*. Whether two nuclei of different sexes are necessary for the formation of an endosperm or not may be left as a unsolved and open question. However, it must not be forgotten that if a male nucleus takes part in the fusion, it may exercise an important influence in increasing the vigour of the fusion product, the reason being that the sperm introduces with itself foreign characters.

In Angiosperms we find that in nearly all the cases the second male fuses with the secondary nucleus of the embryo sac. If we think that a sperm nucleus is necessary to constitute the primary endosperm nucleus, then we cannot consider the formation of a nutritive tissue for the nourishment of the embryo in *E.foliata*, *Welwitschia* and *Gnetum* as an endosperm truly comparable with the endosperm of the Angiosperms.

In *E.foliata* no doubt a sperm fuses with the ventral canal nucleus but there results no special nutritive tissue as an outcome of this process. A sperm therefore does not take part in the formation of nutritive tissue in *E.foliata*. In the case of *Welwitschia* and *Gnetum* there is no fusion of the ventral canal nucleus and the sperm. In *E.foliata*, as well as in *Welwitschia* and *Gnetum* the nutritive tissue results due to the fusion of nuclei in the individual cells of the gametophyte. In Angiosperms the nutritive tissue results from endosperm nuclei and a sperm and not from many fusion nuclei as in *E.foliata*, *Welwitschia*, and *Gnetum*. Thus difficulties arise in considering the nutritive tissue resulting from the fusion nuclei in the Gnetales as a true endosperm comparable with the endosperm of the Angiosperms.

The female gametophyte of the Gnetales furnishes us with a series of very suggestive and interesting facts. Various experiments in nuclear fusion seem to have been tried in all the three genera of the Gnetales, and it is also quite clear that these experiments mostly result in the provision of the nourishment of the egg cell and the growing embryo. Pearson (1929, foot-note, p. 173) has prophesied long before that, " The appearance in *Ephedra* of an endosperm of the same character as that of *Gnetum* is not improbable and its recognition would be of great interest."

The nuclear fusion that is found in the cells of the gametophyte of *E.foliata* is very interesting. However there seems to be nothing very new about it. Nuclear fusion of various kinds is reported and is known in the female gametophyte in the different species of *Ephedra*.

The following are very suggestive facts in connection with the fusion of the nuclei of the cells of the female gametophyte in *E.foliata* which have been observed by other workers on the subject :—

(a) The ventral canal nucleus is capable of fusing with the sperm nucleus. This tendency is found in only a very few Gymnosperms. This phenomenon shows the general tendency of these nuclei to fuse with other nuclei.

(b) In *E.trifurca* an ephemeral group of cells is produced, resulting from the fusion product of the non-functioning male nucleus and the nuclei of jacket cells.

(c) In one example a fusion nucleus was seen fusing with an egg nucleus.

(d) Fusion of the jacket cell nuclei takes place in *E.distachya.* (Berridge and Sanday, 1907).

(e) Jacket cell nuclei enter the egg all from the jacket cells, and fuse within the egg cell in *E.distachya.*

However it must not be forgotten that this fusion of nuclei in the cells of the gametophyte of *E.foliata* takes place on slightly different lines from that of *Gnetum* and *Welwitschia* in both the genera the fusion occurring between the nuclei of the multinucleate cells of the gametophyte, and resulting in uninucleate cells. While in *E.foliata* the fusion of nuclei of the cells of the gametophyte does not always result in uninucleate cells. Even after the nuclear fusion in *E.foliata* the individual cells may have two or sometimes even three nuclei. This is an outcome of the peculiar way in which the fusion takes place. In a cell to begin with there may be a number of nuclei. These nuclei may fuse into a single group or usually in two groups or sometimes in three groups. Due to the stimulus of this fusion between the nuclei of the gametophyte there results a nutritive tissue. Starch is developed in this nutritive tissue for the nourishment of the young developing embryo. (P. M. I.)

It is commonly supposed that the formation of the endosperm takes place in Gymnosperms before fertilization while it takes place in Angiosperms after fertilization. What is said by Pearson (1929, p. 138) about *Gnetum* is equally applicable to the conditions found in *E.foliata.* He says, " The evidence as it stands seems to indicate that in any species fertilization does not necessarily take place at any particular stage in the formation of the endosperm though there may be a tendency to take place before or after this has commenced."

Considerable theoretical interest attaches to the morphology of this nutritive mass which results from the fusing nuclei.

In all other Gymnosperms with the probable exception of *Welwitschia, Gnetum* and *E.foliata* the nutritive tissue is a prothallus. But in all the three above-mentioned plats the conditions are different. The nutritive tissue resulting in these plants from the nuclear fusion cannot be called a prothallium. The reason is obvious. This tissue results

from the fusion of nuclei and consequently the chromosome number of the fusion nuclei is always more than x. So a condition which is necessary to constitute a prothallium is missing.

We cannot also regard this transitory tissue as a sporophyte. Our criterion of the sporophyte being $2x$ number of chromosomes in the nuclei of the cells. The characteristic chromosome number of the sporophyte is not found in these fusion nuclei.

We also cannot regard it as a tissue comparable with the endosperm of the Angiosperms. We know that usually the endosperm of the Angiosperms has a chromosome number which is usually $3x$. We cannot say that this chromosome number is found in these fusion nuclei, since their chromosome number is not constant.

This tissue which is distinct from the gametophyte, the sporophyte and the endosperm, does not interrupt the alteration of generations. In this respect it may be regarded similar to the endosperm of the Angiosperms. It is also the host of the embryonic stage of the next generation. Such a kind of tissue as Pearson (1929) states, must have a distinct morphological status. Pearson calls it " Trophophyte " and defines it as " An endosperm whose primary nuclei are formed by the fusion of the nuclei of potential (or reduced) gametes." It is obvious that *Welwitschia* and *Gnetum* are more allied to each other as regards the female gametophyte than they are allied to the third genus *Ephedra*. Pearson (1929, p. 143) remarks, " A comparison of the gametophytic stages does not at first sight suggest any close degree of affinity." He also states that the remarkable character of the female gametophyte of *Gnetum* and *Welwitschia* to form the trophophyte stands as a marked contrast to that of *Ephedra*. He further mentions that with regard to the other structures in the gametophyte *Ephedra* is much like any typical Gymnosperm, excepting that it is clearly differentiated into distinct regions.

I have described my observations on *E.foliata*, as according to these the female gametophyte gives rise by the fusion of the nuclei in its cells to a nutritive mass which satisfies the conditions for being called a trophophyte.

The relationship of the three genera of the Gnetales are perhaps still as obscure now as they have been at any time. The proof that they are of near affinity is still lacking except a very few things here and there. That this proof has been given at least in some respect by one species, of the genus *Ephedra* is very interesting. If all the species of *Ephedra* are studied with regard to the female gametophyte it will certainly be an important and interesting reading. At least a probability is now opened that in some other uninvestigated species of *Ephedra* there may be found conditions similar to those found in *E.foliata* and also the formation of a trophophyte. If further research fulfils these expectations the gulf as regards the formation of trophophyte between *Ephedra* on the one hand and *Welwitschia* and *Gnetum* on the other will be soon bridged and an important fact as regards the Gnetales will be established.

LIFE HISTORY OF EPHEDRA FOLIATA BOISS
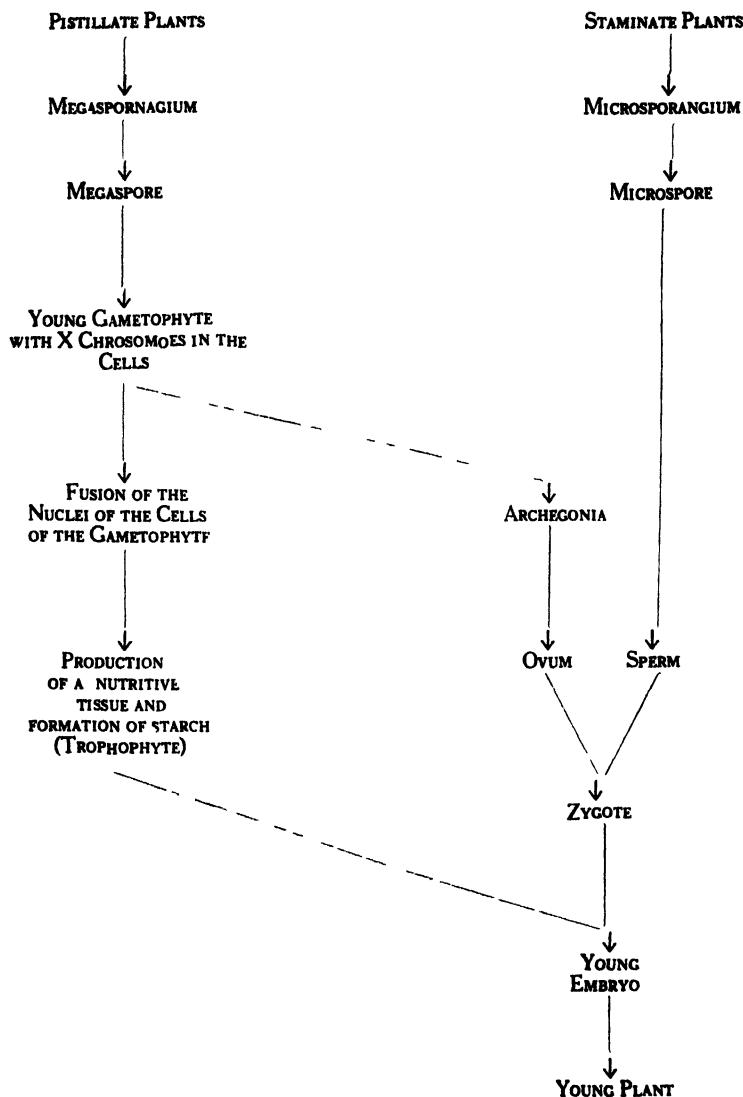
PISTILLATE PLANTS

↓

MEGASPORNAGIUM

↓

MEGASPORE

↓

YOUNG GAMETOPHYTE
WITH X CHROSOMOES IN THE
CELLS

↓

FUSION OF THE
NUCLEI OF THE CELLS
OF THE GAMETOPHYTF

↓

PRODUCTION
OF A NUTRITIVE
TISSUE AND
FORMATION OF STARCH
(TROPHOPHYTE)

STAMINATE PLANTS

↓

MICROSPORANGIUM

↓

MICROSPORE

↓

ARCHEGONIA

↓

OVUM   SPERM

↓

ZYGOTE

↓

YOUNG
EMBRYO

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YOUNG PLANT

ACKNOWLEDGMENTS
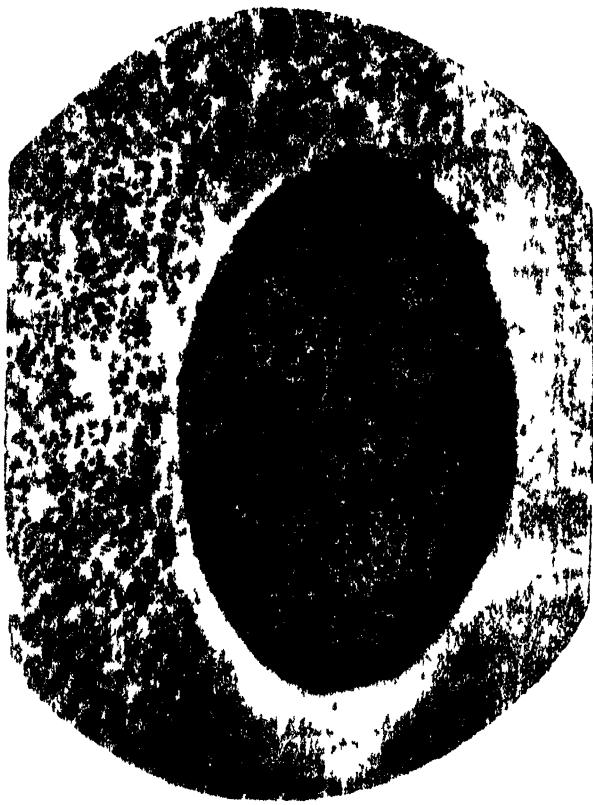
Fig 16. Photomicrograph showing abundant starch in cells The part
with the small cells is the embryo X 150

Fig. 17. Photomicrograph of a section passing through jacket cells.
Nuclei fusing. X 150.

Fig. 18. Photomicrograph showing Nuclei fusing. X 330.

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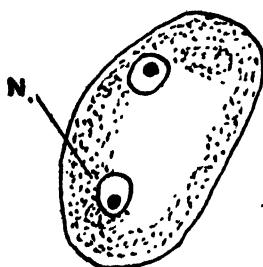
Fig. 1.
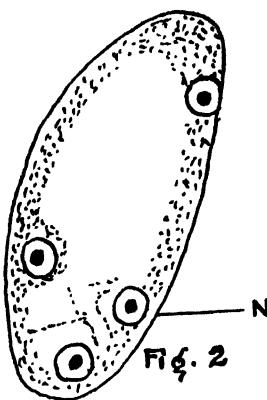
Fig. 2
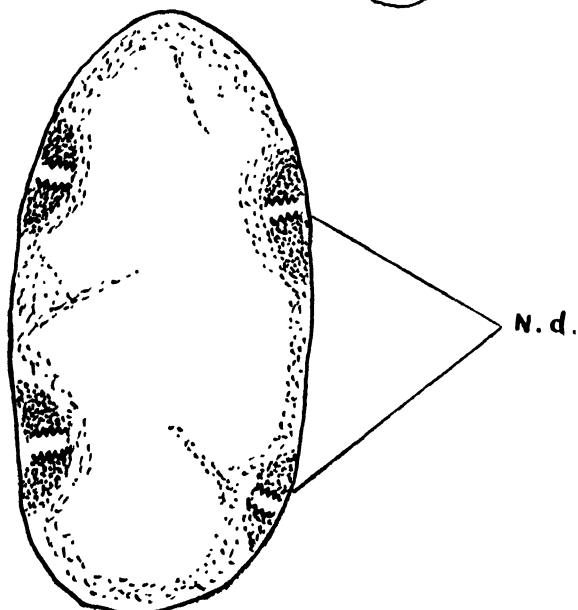
Fig. 3.

Fig. 1. Megaspore with two nuclei.
N, nucleus. X 920.

Fig. 2. Megaspore with four nuclei.
N, nucleus. X 920.

Fig. 3. Megaspore nuclei dividing.
N.d, dividing nuclei. X 920.
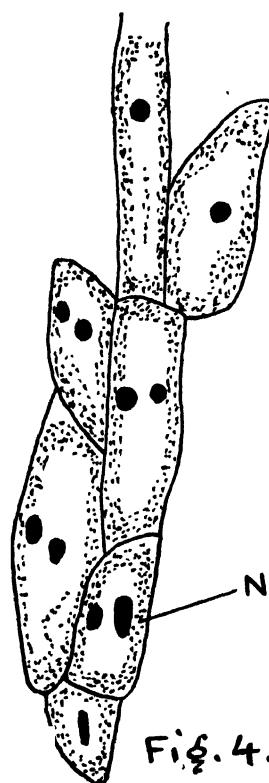
Fig. 4. The region of the gametophyte along which the embryo elongates. X 390.
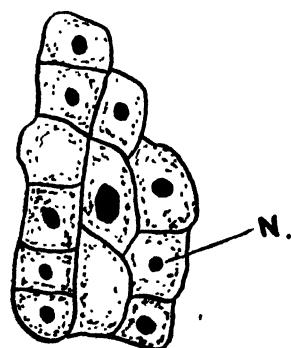
Fig. 5. Cells of the gametophyte towards the chalazal end,
N, nucleus. X 760.
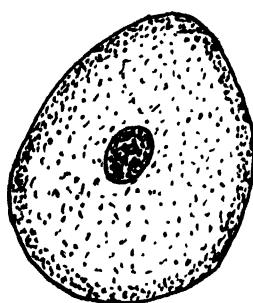
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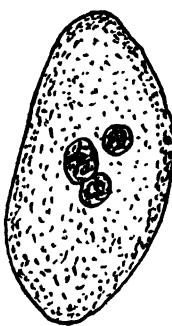
Fig. 7.
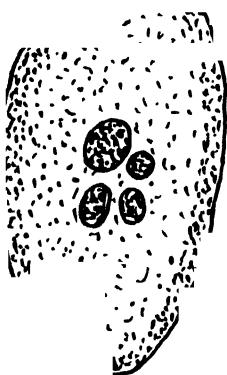
Fig. 8.
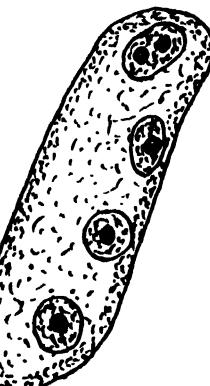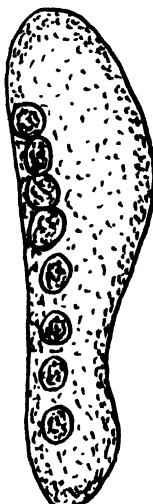
Fig. 9.

Fig. 10.

Fig. 6.   Cell of the gametophyte with one nucleus. X 760.

Fig. 7.   Cell of the gametophyte with three nuclei. X 760.

'Fig. 8.   Cell of the gametophyte with four nuclei. X 760.

Fig. 9.   Same as Fig. 8. X 760.

Fig. 10.   Cell of the gametophyte with eight nuclei. X 760.
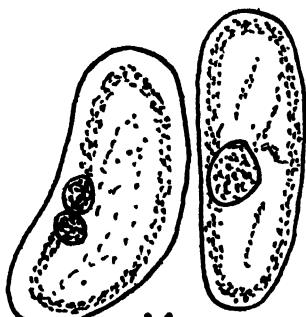
Fig. 11.
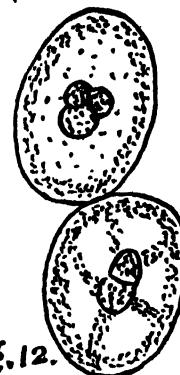
Fig. 12.
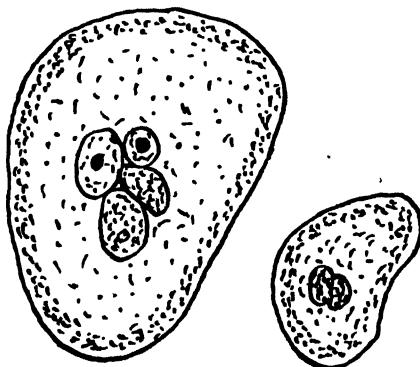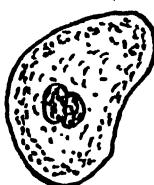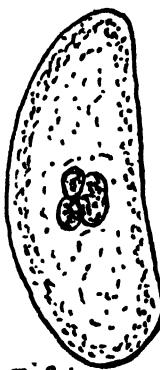
Fig. 13   Fig. 14   Fig. 15

Fig. 11. The cells in the middle part of the gametophyte.
          In one two nuclei are · just fusing, in the other they have
          fused. X 760.

Fig. 12. Three and two nuclei fusing, X 760.

Fig. 13. Four nuclei fusing. X 760.

Fig. 14. Two nuclei fusing. X 760.

Fig. 15. Four nuclei fusing. X 760.

A NOTE ON THE MODIFICATION OF THE LUNG AND THE TRACHEA IN SOME INDIAN SNAKES

By

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IT IS known that except in the Pythons and the Boas which are supposed to be primitive, the right lung is greatly elongated and the left one is either lost or reduced very much. It is also recognised that in some poisonous snakes " the posterior end of the trachea may possess usually on its dorsal side, air cells in its walls and take on the structure of a lung." Since the exact modification of the lung and the trachea in Indian snakes has not received sufficient attention, we have made an attempt to study them in a few snakes and we note below the interesting features observed.

In *Ptyas mucosus* (Figs. 1 and 10) which is non-poisonous, the right lung is well developed, while the left is represented only by a vestige. The trachea is long and just before the heart it divides into two bronchi. The right bronchus enters the lung of its side and by dividing into a number of branches gives rise to the spongy tissue of the lung, while posteriorly it opens into a capacious central sac which acts as a reservoir for the air. The lung is as long as the trachea and extends to the middle of the trunk.

In *Naia tripudians* (Fig. 2) almost a similar condition is found, but the left lung is entirely suppressed and the right lung is distinctly longer than the trachea.

Enhydrina valakadien (Fig. 3) resembles the cobra in the suppression of the left lung, but differs from it and *Ptyas mucosus* in the trachea and the lung being greatly elongated. The lung reaches the cloaca.

In *Distira cyanocincta* (Figs. 4 and 11) the lung is very long as in *Enhydrina* and reaches the cloaca. The trachea however is not long and for most of its length it gives off tiny tracheoles which branch and form secondary lung tissue around it.

In Vipera russelli (Fig. 5) the lung extends to more than half the length of the body and the trachea is almost as long as the lung. That is to say, it resembles Ptyas in the proportional lengths of the trachea and the lung. But secondary lung tissue is developed around the posterior half of the trachea.

In Echis carinata (Figs. 6 and 12) the tracheal lung is as well-developed as in Distira and Vipera and the relative lengths of the trachea and lung are as in *Vipera russelli.*

Gerardia prevostiana (Fig. 7) a non-poisonous snake, resembles *Echis carinata, Vipera russelli* and *Distira cyanocincta* in possessing tracheal lung tissue. Just behind the heart the trachea divides into two bronchi and the right bronchus by dividing into a few bronchioles forms a spongy mass which represents the right lung. The right lung is much more greatly developed than the left, being more elongated.

Cerberus rhynchops (Fig. 8) shows a condition similar to that of *Gerardia prevostiana,* but the left lung is entirely suppressed.

In *Lycodon aulicus* (Fig. 9) the relative lengths of the trachea and the lung are as in Ptyas. There is a vestigial left lung and a well-developed right lung. There is a slight development of the tracheal lung also.

The snakes are carnivorous animals and they swallow prey generally considered large for their size. On account of the large size of the prey the swallowing is slow and breathing becomes impaired. At the beginning of the swallowing the trachea will be pressed at the anterior end and partially choked. At this time the air from the posterior saccular region of the lung is drawn upon. But as the prey is pushed further down they must feel considerable discomfort for want of sufficient fresh air.

Some of the snakes such as Vipera, Echis, Distira, Gerardia and Cerberus possess a modification which mitigates the hardships of swallowing. In these, lung tissue is developed around the trachea and this helps them to breathe air when the prey has been pushed somewhat behind, that is, when the bronchial lung is blocked and its air store is exhausted. The extent of the development of the tracheal lung varies. There is only a slight development of the tracheal lung in Lycodon. It is more developed in Vipera and Echis. It is most developed in Distira. It is also noteworthy that in Distira both the saccular and the tracheal lungs are best developed.

Thus from a comparative study of the trachea and the lung in a few snakes it has been found that there is scope for further investigation. We are pursuing the problem further and the tentative conclusions arrived at now, may require modification.
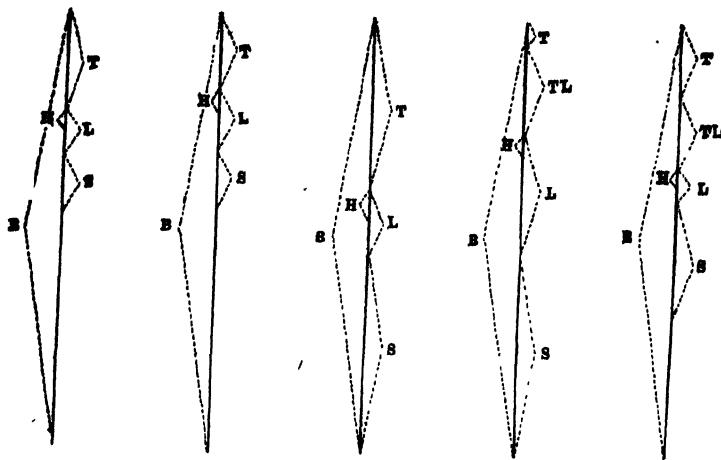
Fig. 1.   Fig. 2.   Fig. 3.   Fig. 4.   Fig. 5.
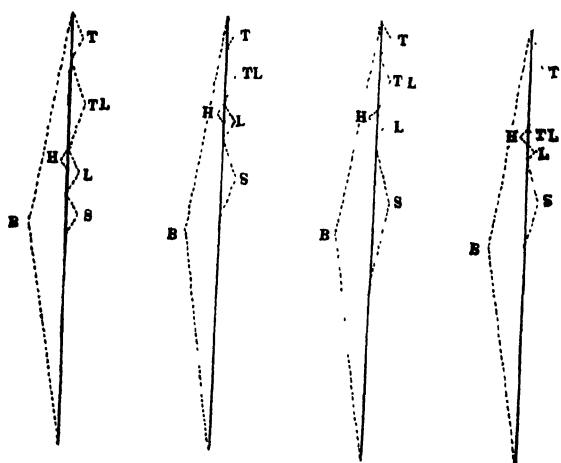
Fig. 6.   Fig. 7.   Fig. 8.   Fig. 9.

Figs. 1—9.—Diagrams showing the relative lengths of the trachea, heart, bronchial, tracheal and saccular lung in the snakes; Fig. 1. *Ptyas mucosus.* Fig. 2. *Naia tripudians.* Fig. 3. *Enhydrina valakadien.* Fig. 4. *Distira cyanocincta.* Fig. 5. *Vipera russelli.* Fig. 6. *Echis carinata.* Fig. 7. *Gerardia prevostiana.* Fig. 8. *Cerberus rhynchops* Fig. 9. *Lycodon aulicus.* T—Extent of trachea. H—Length of the heart. B—Length of the body. L—Extent of the Bronchial lung. TL—Extent of the Tracheal lung. S—Extent of the Saccular lung.
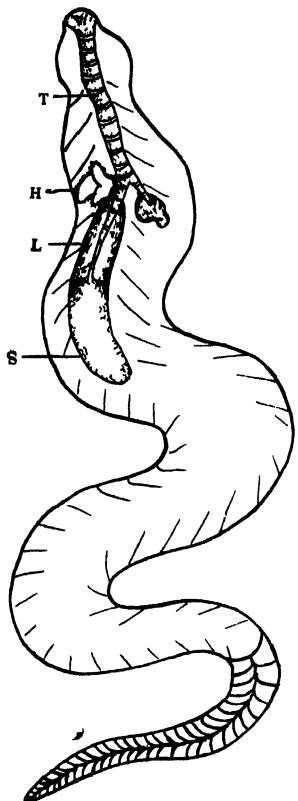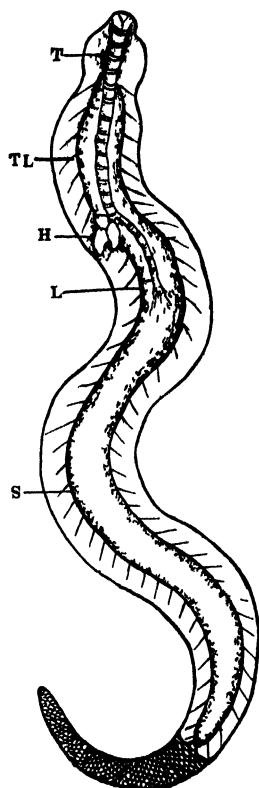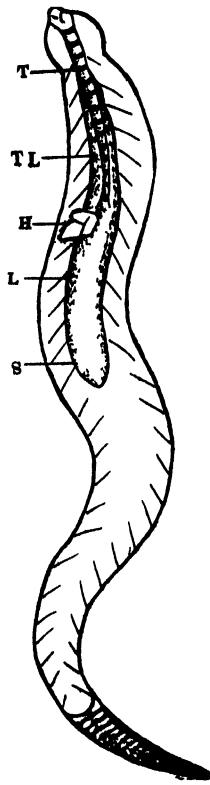
Fig. 10.   Fig. 11.   Fig. 12.

Fig 10. Sketch showing a dissection of the trachea, lung and heart in *Ptyas mucosus*.
Fig. 11. Sketch showing a dissection of the trachea, lung and heart in *Distira cyanocincta*,
Fig. 12. Sketch showing a dissection of the trachea, lung and heart in *Echis carinata*.
T—Trachea. H—Heart. L—Bronchial lung. S—Saccular lung. TL—Tracheal lung.

CARBOHYDRATES IN FRUITS

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CARBOHYDRATES are the chief nutritive materials in the fruits. In ripe fruits they are wholly in the form of soluble sugars. Starch is often found in unripe fruits, notably in ordinary plantains. Along with starch, sucrose, glucose and fructose are also found in sufficient quantities in fruits.

In the present investigation an attempt has been made to estimate quantitatively the different types of sugars.

EXPERIMENTAL

Plantains of a definite age were obtained from a single source wherever possible. For comparison of the results of analyses, plantains having the same coefficient of ripeness were selected. The coefficient of ripeness was calculated as was done by Ranganathan (Jour. Ind. Inst. of Science, Vol. II, Part VII, pp. 75–83), viz., $\frac{\text{weight of the pulp}}{\text{weight of the peel}}$. The coefficient of ripeness was found to vary with different varieties of plantains, but the above method was used for all the varieties. In cases other than plantains, such as chiku, apple, orange, etc., the above method was found to be unsatisfactory. Here preliminary experiments were carried out to determine the maximum amount of total reducing sugars obtainable in a fruit. Those fruits having the same concentration for total reducing sugars were selected for analysis.

EXTRACTION AND CLARIFICATION

G. J. Fowler and T. Dinanath (Jour. Ind. Inst. of Science, Vol. 6, Part VII, pp. 131–145) and E. Widdowson (Biochem. J., 1935, 150–155) used alcohol for extraction of available carbohydrates in different fruits. The use of alcohol as a solvent for extraction of sugars from biological material prevents fermentation of the extract and also precipitates other materials such as proteins. In spite of above advantages alcohol has been replaced by distilled water in the present investigation for the following reasons :—

(1) As alcohol is a very expensive reagent it was thought desirable to replace it by water. With this end in view extracts of fruits with alcohol and with water were analysed and the results of analyses of the respective extracts were compared. It was found that no difference existed between the values obtained in alcohol and in water extract.

(2) As the estimation of sugars was carried out in one day there was no need to use alcohol for fear of fermentation.

Clarification was effected by precipitating the proteins, etc., by using basic lead acetate solution. Excess of lead was removed by di-sodium hydrogen phosphate carefully avoiding the addition of excess of the latter reagent.

ESTIMATION OF TOTAL AND FREE REDUCING SUGARS

Charles F. Poe and F. G. Edson (Ind. Eng. Chem. Anal. Ed., Vol. IV, No. 3, 1932, 300–302) have estimated reducing sugars in food materials. In the same manner, 1 c.c. of the clarified solution calculated to contain about 0·002 gms. of reducing sugars was taken in a test tube and to it 3 c.cs. of the solution (containing 0·8 per cent., 2 : 4. dinitrophenolate, 1 per cent. sodium hydroxide, 0·25 per cent. phenol and 10 per cent. rochelle salt) were added. The tube was heated in a boiling water bath for 6 minutes and cooled in running water from a tap for 3 minutes, the violet colour of the solution is then compared with that developed by the standard solution of a reducing sugar (glucose 1 c.c.=0·002 gms.) similarly treated.

Another portion of the extract calculated to contain 0·004 gms. of reducing sugars was then subjected to hydrolysis by 2 c.c. of 8 N. HCl for the estimation of total reducing sugars. The difference between the total reducing and the free reducing sugars gave the amount of non-reducing sugars present in the extract.

After determining the total and free reducing sugars (glucose and fructose) present in the extract, a further attempt was made to estimate glucose, and fructose separately.

GLUCOSE

Glucose was estimated by using the Iodine titration method of R. E. Lothrop and Holmes (Ind. Eng. Chem. Anal. Ed., Vol. 4, No. 3, 1931, 334–339) with this modification, namely, that the time allowed for oxidation of glucose was brought down from 10 to 6 minutes to avoid errors due to simultaneous oxidation of fructose. 40 c.cs. of the clarified solution calculated to contain 0·04 to 0·05 gms. approximately of glucose were taken in a flask ; 40 c.cs of 0·05 N iodine solution and 25 c.cs. of 0·1 N sodium hydroxide solution were added one after another, mixed thoroughly and kept in a water bath at 20°C for 10 minutes. The mixture was then acidified with 5 c.cs of 2 N sulphuric acid and titrated against N/20 sodium thiosulphate.

FRUCTOSE

Fructose was estimated by Seliwenoff's method as well as Diphenylamine. method (W. W. Oppel, Biochem. J., 1930, 229, 85–89). These methods gave identical results. Seliwenoff's method is much more simple than the Diphenylamine one, as the latter requires elaborate procedure of extraction of the colour developed with alcohol. 1 c.c. of the clarified solution containing not more than 0·002 gms. of fructose was taken in

a boiling tube. 5 c.c.s of the Seliwenoff's reagent (containing 0·025 gms. of resorcin in 100 c.c.s of 50 per cent. HCl) were then added to it. The colour developed by the solution on keeping it in a boiling water bath for seven minutes and cooling, was then compared with the standard similarly treated.

CANE SUGAR

As for non-reducing sugars, there was no indication of the presence of any type other than cane sugar. The amount of cane sugar in the solution was obtained by the difference between the total reducing sugars and the free reducing sugars as stated previously.

STARCH

Starch was estimated as follows :—

First the total reducing sugars were determined in water extract as mentioned above. Then a fresh quantity about 1 to 2 gms. of the edible of portion of the fruit was accurately weighed and was hydrolysed by 2 c.cs. of 8 N. HCl directly. The total reducing sugars in the hydrolysed portion were then estimated (the treatment of the edible portion with acid brings about the hydrolysis of starch). The difference between the total reducing sugars in the hydrolysed pulp and that present in water extract gave the amount of starch present in the fruit. It may be mentioned here that the water extract did not show the presence of starch on careful analysis.

The results obtained for different types of sugars in various fruits are given in Tables 1 and 2.

TABLE No. 1

Amount of Different Sugars in gms. per 100 gms. of Fruit

Plantain (Velchi).

Coefficient of ripeness	Free reducing sugars	Total reducing sugars	Glucose	Fructose	Cane sugar (By difference)	Starch	Total Carbo- hydrates
2·31	2·79	5·00	1·72	0·98	2·099	13·9	18·90
2·98	5·10	11·73	2·78	2·30	6·30	7·17	18·95
3·60	6·90	13·51	3·98	2·79	6·27	5·39	18·99
4·40	10·20	17·50	5·50	4·68	6·93	1·40	18·89
5·38	11·56	17·89	6·09	5·41	6·01	1·01	18·92
5·90	12·14	17·94	6·39	5·60	5·46	0·96	18·93
6·10	12·4	18·50	6·29	5·82	5·79	0·40	18·90

TABLE No. 2

Amount of Different Types of Sugars in gms. per 100 gms. of Fruit

Variety of sample	Total reducing sugars	Free reducing sugars	Glucose	Fructose	Cane sugar (By difference)	Starch	Total Carbo-hydrates
Plantain (Green skinned) (Musa Sapientum)—Kela.	18·33	11·57	6·32	5·28	6·42	0·50	18·83
Plantain (Rasbali) (Musa Sapientum)—Kela.	18·45	11·68	6·22	5·51	6·52	0·29	18·74
Plantain (Velchi) (Musa Sapientum)—Kela.	18·66	11·72	6·31	5·67	6·61	0·49	19·15
Guava (Psidium Guyava)—Peru—Amrud.	9·44	4·72	2·40	2·31	4·48	0·21	9·65
Orange (Juice) (Citrus Aurantium)—Santra.	8·31	4·38	2·18	2·16	3·73	Nil	8·31
Apple (Red) (Pyrus Malas) Seb—Safarchand.	10·48	7·44	1·56	5·99	2·88	..	10·48
Apple (Yellow) (Pyrus Malas) Seb—Safarchand.	10·50	7·62	1 66	5·93	2·63	..	10·50
Figs (Ficus Carica)—Anjeer.	9·10	9·07	4·89	4·11	Nil	..	9·10
Grapes (Black) (Vitis Vinifera)—Draksha.	14·22	14·19	7·48	6·70	..	..	14·22
Grapes (Greenish white) (Vitis Vinifera)—Draksha.	14·78	14·69	7·62	7·24		..	14·78
Sapota (Sapota Zapotilla)—Chiku.	9·21	6·31	2·80	3·44	2·75	..	9·06

N.B.—The mean of 8 samples of each variety is tabulated here.

The English, Botanical as well as Local names for the fruits are given in the first column.

DISCUSSION

A close examination of the tables reveals certain interesting points regarding the distribution of the different types of Carbohydrates.

It may be noted that the amount of starch in all the fruits except plantain, does not exceed even 1 per cent. of the total fruit pulp when ripe and in an eatable condition.

In the case of plantains, the amount of starch is found to vary considerably depending on the stage of ripeness. It is about 14 per cent. in the case of unripe plantains and this starch decreases with progressive ripeness. It will be seen from the Graph No. 1, that the amount of starch decreases as the coefficient of ripeness increases. It is also noticed that with progressive ripeness the amounts of fructose and glucose are increased. It could also be seen from Table No. 1 that for the loss of 6·73 per cent. of starch, the increase in glucose and fructose taken together is 2·38 per cent. and in cane sugar 4·42 per cent. This is an indication, no doubt, that the starch is converted quantitatively to glucose, fructose and cane sugar.

Graph 1
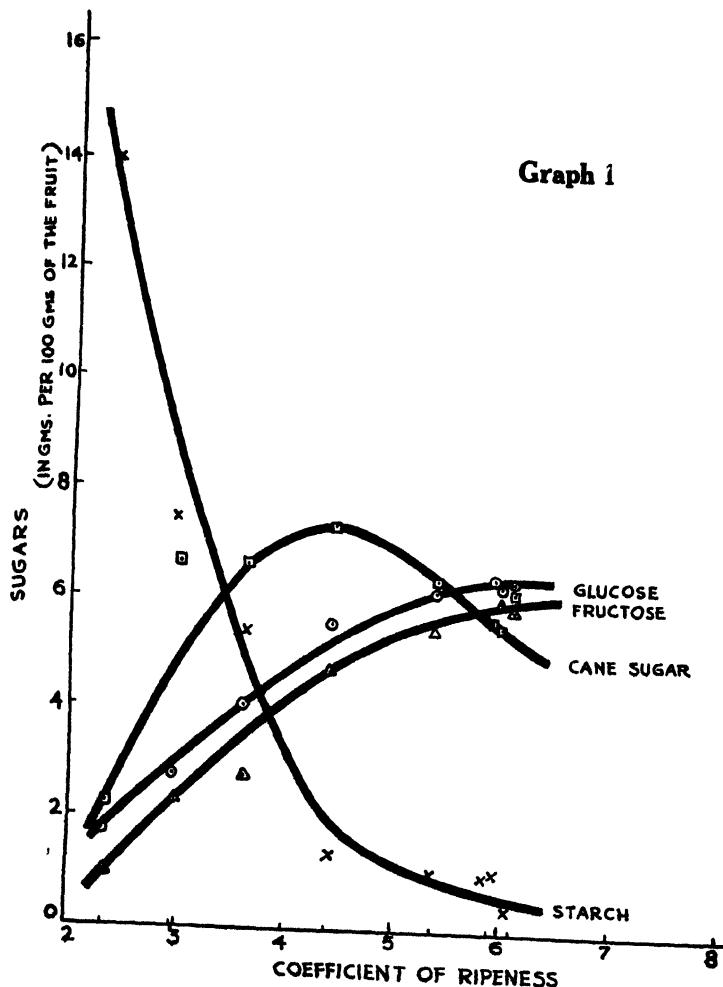
Cane sugar is present to the extent of 6–7 per cent. in plantains, while it is completely absent in figs and grapes. The amount of cane sugar in apples, chiku, orange and guava varies roughly from 3 to 4 per cent. Glucose and fructose are present to the extent of 6 per cent. and 5·5 per cent. respectively in plantains. The amount of fructose in apples is about 3½ times that of glucose ; while in figs and grapes the amounts of glucose and fructose are nearly the same.

E. Widdowson and R. A. McCance (Biochem. J., Vol. XXIX, Part I, 1935, 151–156) have worked on some of the fruits such as apples, bananas, orange juice, etc. Their figures for sugars are comparable with the results recorded here. Their values for the bananas differ from the values of plantains in the present investigation. The difference may be due to the fact that they have used fresh raw bananas while in the present investigation ripe plantains having the coefficient of ripeness of 2·7 to 2·8 in the case of green skinned and 6·1 to 6·2 in case of velchi plantains were selected. At these stages starch is found to be in very small quantity as most of it has been completely converted to soluble sugars.

Plantains when ripe are very rich in soluble sugars, containing about 17 to 19 per cent. while grapes come next with 14 per cent. Orange juice contains about 8 per cent. while apples, guava, chiku and figs contain about 9 to 10 per cent.

SUMMARY

1. The amounts of different types of sugars in 11 fruits are given.

2. Colorimetric method proposed by Poe and Edson (Loc. Cit.) for the estimation of reducing sugars in food-stuff is tried.

A NOTE ON THE DEGENERATION OF GILLS IN AIR-BREATHING FISHES

By

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IT IS generally believed in zoological circles and is often emphasized that " the aerial respiration in fishes has been primarily an adaptation to life in a medium poor in oxygen." The fact that air-breathing fishes are found to live along with water-breathing ones, throws some doubt on the accuracy of that statement, for animals exclusively adapted for certain habitats are found in those habitats only. On making a comparative study of the gills (Fig. 1) of some of the fishes available locally, our grounds for doubting that statement are further strengthened.

In all, 14 species of fishes were examined. Of these, five (*Therapon jarbua, Sparus berda, Sillago sihama, Nematalosa nasus* and ·*Stromateus cinereus*) are common marine fishes. Of the nine species of fresh-water fishes examined, six (*Anabas scandens, Haplochilus lineatus, Polyacanthus cupanus, Saccobranchus fossilis, Ophiocephalus striatus,* and *Osphromenus gourami*) are air-breathers. The others (*Rasbora daniconius, Barbus vittatus,* and *Etroplus maculatus*) are water-breathing forms. The following procedure has been adopted in order to estimate the respiratory efficiency of the gills. Since the respiratory efficiency of a gill must be directly proportional to the gill surface—all other things remaining constant—the total area of the gill surface was ascertained. This is arrived at by multiplying the mean length and breadth of a gill filament first and again multiplying that product with the total number of filaments present. The number thus obtained is the total area of the gill surface in a fish. The thickness of the gill filament is regarded as negligible. In some fishes folds are developed on the filaments and these must to some extent increase the gill surface exposed. The oxygen required is taken to be roughly proportional to the volume of the fish. The gill surface required for unit volume, that is, one cubic centimetre is then ascertained. The gill surface thus

obtained for water-breathing fishes is regarded as the standard. The following table gives details of the gill structure and the gill surface per unit volume in the fishes examined :—

Name of the Fish	Volume of the fish in c.c.s.	Number of pairs of gills	Total number of gill filaments	Nature of gill filament	Area of each gill filament. Length × breadth in mms.	Total area of gill filaments in sq. mms.	Area of the gill surface per unit volume in sq. mms.
1. *Rasbora daniconius.*	9·5	4	992	Many long folds.	2·24 × ·3	665	70
2. *Barbus vittatus* ..	1	4	512	Many short folds.	1 × ·15	76·5	76
3. *Etroplus Maculatus.*	6	4	1,088	No folds ..	2·0 × ·2	435	72
4. *Therapon jarbua.*	19	4	1,520	Many long folds	2·8 × ·35	1,390	78
5. *Sparus berda* ..	18	4	1,600	No folds ..	3·5 × ·225	1,260	70
6. *Sillago sihama* ..	13	4	1,440	Do. ..	2·5 × ·275	990	76
7. *Nematalosa nasus.*	27	4	1,680	Many long folds.	3·5 × ·3	1,763	65
8. *Stromateus cinereus.*	180	4	1,520	Many long folds, confined to one side.	12 × ·7	12,768	71
9. *Anabas scandens.*	4	3	640	No folds ..	1 × ·1 & 2 × ·15	152	38
10. *Haplochilus lineatus.*	2·0	4	800	Few folds ..	1 × ·1	80	40
11. *Polyacanthus cupanus.*	1·5	4	480	Some long folds.	·75 × ·1	36	24
12. *Saccobranchus fossilis.*	15	4	448	Do. ..	2·5 × ·33	358	24
13. *Ophiocephalus striatus.*	2·0	4	480	Do. ..	75 × ·2	72	36
14. *Osphromenus goarami.*	180	4	1,888	No folds ..	4·5 × ·5	4,248	24

From the table, the gill surfaces for unit volume of the marine fishes are found to be between 65 and 78 sq. mms. The gill surfaces per unit volume in water-breathing fresh water fishes are between 70 and 76 sq. mms. The corresponding figures for the air-breathing fishes are between 24

and 40 sq. mms. The presence of folds on the filaments should increase the gill surface of those species in which they are met with. From these figures one thing is certain. The respiratory capacity of the gills of air-breathers is very much less than that of other fishes. It means their gills are under-sized. The accessory respiratory organs obviously supplement the gills.

If aerial respiration has been primarily an adaptation to life in a medium poor in oxygen, such fishes must be confined to certain pools and marshes and one would not expect to find them along with other fishes. But that does not seem to be the case anywhere. Carter and Beadle (1931) who studied the fish fauna of the swamps of the Paraguayan Chaco found that of the 20 species of fishes inhabiting the swamps, only eight were air-breathers. The fresh water fishes examined by us are also from a single pond in Bombay.

Hora (1935) studied the fishes of the torrential streams and found that the gills were degenerate in those. He takes degeneration to be an adaptation to water containing more oxygen than usual. If the presence of more oxygen in the waters brings about degeneration of the gills, the reaction to less oxygen in the waters should be their extra developments Degeneration of the gills under the circumstances therefore can not be attributed as a reaction to a medium deficient in oxygen.

On the other hand, if the development of accessory respiratory organs and the degeneration of gills are to be thought of in terms of mutations, a more logical explanation on the origin of these two changes is possible. They must have taken place side by side ; as the accessory respiratory organs strengthened, the gills declined. Suppose that in the ancestors of these fishes two mutations, one involving the development of an air-breathing organ, and the other involving the degeneration of the gills occurred, some time in the distant past. If the mutants were viable the population in the transitional days that followed must have been composed of four kinds of individuals :—

    (1) Those without either of the two mutations.

    (2) Those with the normal gills and the mutation involving the development of accessory respiratory organs.

    (3) Those with the mutation involving the degeneration of the gills, but without the mutation involving accessory respiratory organs.

    (4) Those with both mutations.

There must have been in the population heterozygous forms also. It is obvious that the third group must have had no chance of survival. The second group must also have succumbed, since the development of accessory respiratory organs involved diversion of energy without corresponding benefit. The first and last groups must have had better chances of survival, and we may take that the present day air-breathing fishes are the descendants of the fourth group. We do not mean that

the complicated air-breathing organs came into existence at a single stroke. They must be the result of many progressive mutations. In the light of our studies, the general impression that the accessory respiratory organs have come about as an adaptation for life in a medium poor in oxygen seems to us untenable.

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Since Das B. K. gives a complete list of literature it is omitted here.

Fig. 1

A

B

C

D

E

F

G

A—A part of a gill filament of Rasbora daniconius.
B—A gill filament of Barbus vittatus.
C—A part of a gill filament of Etroplus maculatus.
D—A part of a gill filament of Therapon jarbua.

E—A part of a gill filament of Sparus berda.
F—A part of a gill filament of Sillago sihama.
G—A part of a gill filament of Stromateus cinereus.
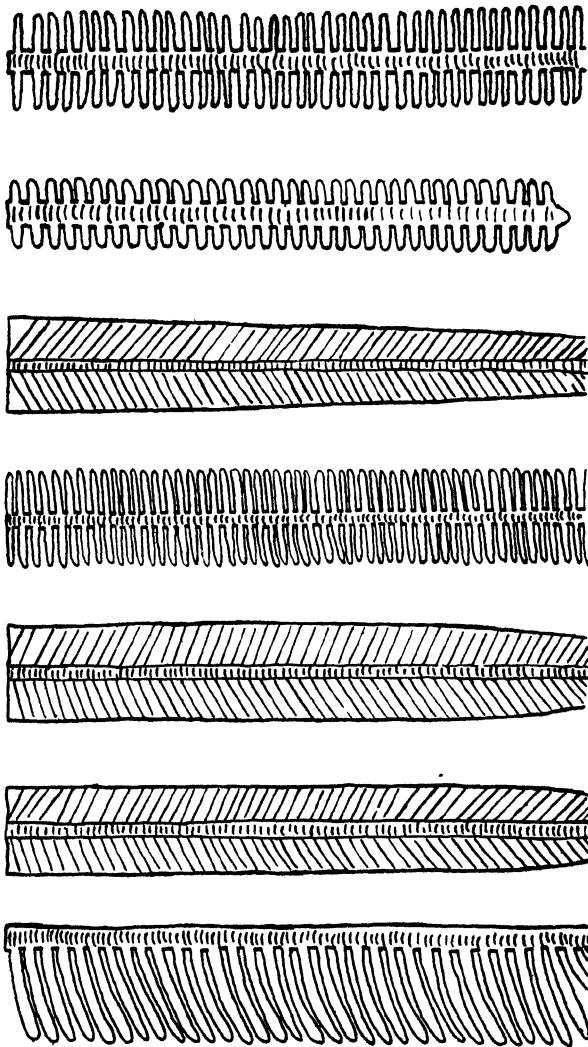
Fig. 1—contd.

H—A part of a gill filament of Nematalosa nasus.
I—A gill filament of Anabas scandens.
J—A gill filament of Haplochilus lineatus.
K—A gill filament of Polyacanthus cupanus.

L—A part of a gill filament of Saccobranchus fossilis.
M—A gill filament of Ophiocephalus striatus.
N—A part of a gill filament of Osphromenus goureami.
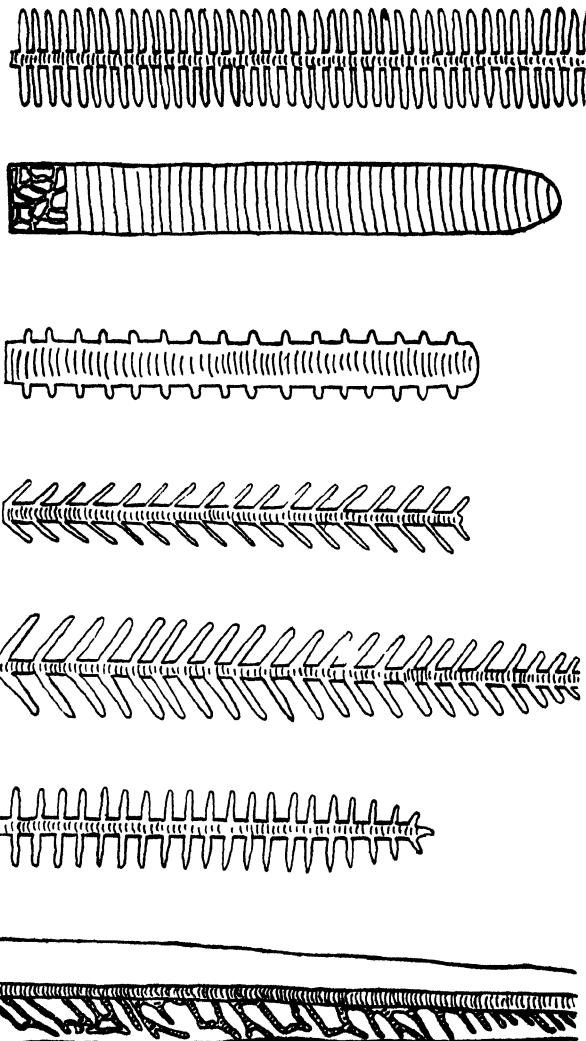
Indian Ecological Society ·

On 6th January, 1941, at the time of the meeting of the Indian Science Congress Association held at Benares, the above Society was inaugurated.

Its object is to cultivate and promote the study of plant and animal ecology by close co-operation with various scientists like the Botanist, the Zoologist, the Geologist, the Meteorologist, the Agriculturist, the Soil Scientist, the Chemist and the Geographer.

At the inaugural meeting the following were elected office-bearers of the Society for 1941 :—

President.—Professor S. P. Agharkar of the Calcutta University.

Vice-Presidents.—Dr. N. L. Bor, I.F.S., of Forest Research Inst. and College, Dehra Dun.

Dr. S. L. Hora of the Zoological Survey of India, Calcutta.

Secretary and Treasurer.—Dr. F. R. Bharucha of Bombay.

Members of the Executive Committee.—Mr. P. W. Davis, I.F.S., of Ootacamund ; Prof. P. W. Gideon of Karnatak College, Dharwar ; Dr. R. D. Misra of T. N. J. College, Bhagalpore ; Dr. L. A. Ramdas of the Observatory, Poona ; Dr. T. S. Sabnis of Cawnpore.

The subscription of the Society is fixed at Rs. 3 only per annum and anybody interested in it may apply to the Honorary Secretary, Royal Institute of Science, Bombay 1.

Review

This book, written by the very eminent technicien Dr. Johansen, stands unique in the field and no person doing botanical research can afford to be without it. It contains in a comprehensive form the results of research end experience extending over a number of years. The value of the book is all the more increased because only methcds which have been fully tested and proved to be successful are includ d. The first section of the book describes the apparatus, reagents, killing and fixation, stains, staining procedures, special methods, whole mount methods, glycerine method, collo'd n methods, paraffin methods, smear methods, cytological methods and microchemical methods. There is also a small chapter giving the addresses of a number of firms which supply reliable biological material and apparatus.

In the second section, are dealt with all the plent phyla in phylogenetic order, and gives very detailed directions for handling the material. There are also extremely useful instructions for collection, preservation and cultivation of plants and plant material. There are 110 figures, most of them be'ng photomicrographs. The book is equally valuable to the beginner as well as to the most advanced worker. Chapters on photomicrography and palæobotenical technique are lacking in the book and we hope that these also will be included in a later edition. It is a credit to the publishers that they have made such an excellent work available to botanists.

<div align="right">V. S. R.</div>

List of Theses in Botany and Zoology which have been accepted in lieu of the Examination for the Degrees of M.Sc. and Ph.D. from March to September 1941.

Name of the Candidate.	Title of the Thesis.	Teacher.	Place of Research.	Remarks.
	M.Sc.			
	Botany			
Bhavnani, G. D. ..	A contribution to the floral organogeny, structure and development of the micro — and mega—spores, their gametophytes and embryology of Aristolochia bracteata Retz.	B. N. Mulay, Esq. ..	D. J. S.	
Samarth, K. D. (Mrs. Ranadive).	Micro — and Mega—sporogenesis in the genus Anona and cytological investigations in the genus Cyanotis.	Professor L. S. Kumar.	College of Agriculture.	One part under the new title " A Cytological Study of the Genus Anona " appears in this issue.
	Zoology			
Bagal, S. R. ..	Study on some coccinellid beetles and their economic importance.	Professor V. G. Deshpande.	Do.	
	Microbiology			
Bhat, J. V. ..	A comparative study of the chemical and microbial action on nitrogen status of soil.	The Rev. G. Palacios, S.J.	St. Xavier's College.	
Vachha, S. B ..	A physiological and chemical study of Indian Bacteria.	Do.	Do.	
	Ph.D.			
	Botany			
Navalkar, B. S. ..	Studies in the Ecology of the Mangroves of the Bombay and Salsette Islands.	Dr. F. R. Bharucha..	R. I. Sc.	.. Papers I and II published in the Journal of the University of Bombay, Vol. VIII, 5 (1940), and Vol. IX, 5 (1941), respectively.
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SCIENCE NOTES :

Physics

NOTICE

This issue completes Volume X (New Series) of the Journal. The Title Page and Index will be sent in due course.

Manager

Similarly it will be seen that $\frac{21}{81}=.259259259\ldots$, $\frac{48}{81}=.592592\ldots$, $\frac{75}{81}=.925925925\ldots$. Again the same cyclic law holds true for these numbers. $\frac{12}{81}=.148148\ldots$, $\frac{39}{81}=.481481\ldots$, $\frac{66}{81}=.814814\ldots$, and give confirmation of the statement. All these values of M discussed so far have their digital root* 3. These are arranged in a table to show the recurring part they would give if divided by 81.

TABLE I

For M with digital root 3

0^8	3^{80}	7^{57}	
1^{12}	4^{89}	8^{66}	
2^{21}	5^{48}	9^{75}	

The method of looking at the table is best given by finding the value for 39   Here 39 occurs in column 2 with 4 below it and we write the figures in the row in cyclic order beginning with 4. Thus 481 is the recurring part in $\frac{39}{81}$.

A similar table for M with digital root* 6 can be constructed.

TABLE II

For M with digital root 6

0^6	7^{60}	4^{33}	
1^{15}	8^{69}	5^{42}	
2^{24}	9^{78}	6^{51}	

e.g., we shall find the recurring part of 42 by means of this table. Here 42 is in the last column with 5 below it. We write therefore the figures in this row in cyclic order beginning with 5. Hence 518 is the required recurring part.

(c)   When M is neither a multiple of 3 nor 9. In this case the recurring period consists of nine digits, e.g., $\frac{1}{81}=.012345679$ giving also the recurring period of other numbers with digital root 1 with necessary cycle consideration.   Thus $\frac{19}{81}=.234567901\ldots$. An investigation carried out with all numbers M neither multiples of 3 nor 9, gives the following table.

---

*The digital root means the remainder left when the number is divided by 9.

Table III

When M is neither a multiple of 3 nor 9

Digital root of M									
1	0^1	1^{10}	2^{19}	3^{28}	4^{37}	5^{46}	6^{55}	7^{64}	9^{73}
2	0^2	2^{20}	4^{38}	6^{56}	9^{74}	1^{11}	3^{29}	5^{47}	8^{65}
4	0^4	4^{40}	9^{76}	3^{81}	8^{67}	2^{22}	7^{58}	1^{13}	6^{49}
5	0^5	6^{50}	1^{14}	7^{59}	2^{28}	8^{68}	3^{22}	9^{77}	5^{41}
7	0^7	8^{70}	6^{52}	4^{81}	1^{16}	9^{79}	7^{61}	5^4	3^{25}
8	0^8	9^{80}	8^{71}	7^{62}	6^{53}	5^{44}	4^{35}	3^{26}	2^{17}

As an illustration of the use of table III, we find the recurring period for $\frac{68}{81}$. Here digital root of 68 is 5. It is not a multiple of three or nine. For digital root 5 in the table we find below 68 the figure 8. Hence we take all the figures in that row beginning with 8. Thus the recurring part in $\frac{68}{81}$ is 839506172. For $\frac{74}{81}$ we find from digital root 2, the recurring part to be 469135802.

(3) All the 81 values of M possible are considered.

9 values when M is a multiple of 9,

18 values when M is a multiple of 3 but not cf 9,

54 values when M is neither a multiple of 3 nor 9.

And these are all the values that we require.

(4) A few preparations are made before we write the required product of $W_n^9 \times N$.

Express $\frac{N}{81} = Q + \frac{M}{81}$ where Q is an integer and M < 81 and find the recurring part of $\frac{M}{81}$ and write it in nine digits. Thus, e g.,

when M= 9 the recurring part is 111111111

   ,,   27 the recurring part is 333333333

   ,,   15 the recurring part is 185185185

   ,,   48 the recurring part is 592592592

   ,,   17 the recurring part is 209876543

   ,,   37 the recurring part is 456790123.

This number so written we shall call L.

(5) Obtain a new number from this number L by subtracting every digit from 9 in order. We shall call this number as complement of L and denote it by L^1. Thus complement of 185185185 is 814814814.

(6) Subtract $Q+1$ from L and add $Q+1$ to L^1 and we call these numbers as T and T^1. Then write the number $QT(9)_{n-1} T^1$ and subtract from this the number Q with its unit digit beginning with the last 9 (the right hand side) in the central part in this number and we get the required product $W^0_n \times N$.

Example I. Let us find the value of $W^9_5 \times 895$. Here N=895, Q=11, M=4.

Recurring part for 4 is 049382716 = L

Its complement is   950617283 = L^1

$Q+1 = 12$.   L—12   = 049382704 = T

          L^1+12 = 950617295 = T^1

                 and $n—1 = 4$

Hence $QT(9)_{n-1} T^1$ is $1104938270499999950617295$

                        11

Subtracting Q=11 as noted above the product is
11 0493827049988 950617295.

Example II. To find the value of $W^9 \times 48324$.

Here N = 48324, Q = 596, M = 48.

Recurring part for 48 is 592592592 = L

Its complement is   407407407 = L^1

$Q+1 = 597$

$L—597 =$ 592591995

                      $n—1 = 1$

$L^1+597 =$ 407408004

Hence $QT(9)_{n-1} T^1$ is 5965925919959 407408004

                      596

Subtracting Q as indicated, the product is
596 5925919363 407408004.

(7) If $n=1$ then $n—1=0$ and no nine is to be written after L. Hence from L we have to subtract $Q+1$ and Q again, *i.e.*, we subtract $2Q+1$ and the product can be written out, *e.g.*, $W^9_1 \times 17452$.

Here Q=215,   M=37.

The recurring part for 37 is 456790123 = L

Its complement is   543209876 = L^1

$n—1 = 0$;   Hence $Q+1 = 216$, $2Q+1 = 431$.

∴ $L—431 = 456789692$

  $L^1+216 = 543210092$

And the product is 215 456789692 543210092.

(8) When N is less than 81 the case becomes more simple. We get Q=0, $Q+1=1$ and we have only to subtract and add one to L and L^1 and write $T(9)_{n-1} T^1$ as the product.

Thus $W_2^2 \times 52$ gives for the recurring part of 52,

$$L = 641975308$$

$$n-1 = 3$$

$$L^1 = 358024691$$

Hence as Q is zero the product is

$$\underline{641975307} \ \underline{999} \ \underline{358024692}$$

by adding and subtracting one from L^1 and L.

(9)   When N is an exact multiple of 81 the process becomes interesting, e.g., N=10287, then when divided by 81 the quotient is 127. In this case take Q=126 and M=81, i.e., take 81 as the remainder and the corresponding recurring part $(9)_9$ is taken and the process then continued as before.

e.g., to find $W_2^0 \times 10287$

We take Q=126   L =999999999

$$L^1 = 000000000$$

$$Q+1 = 127$$

$$L - 127 = 999999872 = T$$

$$n-1 = 1$$

$$L^1 + 127 = 000000127 = T^1$$

$$\therefore QT(9) \ T^1 = 126999999872\,9000000127$$

$$126$$

Hence subtracting Q=126 as indicated, the product is

$$\underline{126} \ \underline{9999998603} \ 000000127.$$

It may be noted that W_1^0 is the ordinary wonderful demlo-number already referred to. The theory of such products is very interesting and will be discussed at some later date.

College of Engineering, Poona—
    Khare's Wada, Camp Deolali.

THE VALUE OF √2 GIVEN IN THE ŚULVASUTRAS

By

PROFESSOR L. V. GURJAR, M.A.

ŚULVASUTRAS are the supplements of the Kalpasutras and give systematically arranged descriptions of sacrificial rites which had been practised in India in Vedic age. They are the works composed in a period between 1500 B C. and 750 B C. (Winternitz: History of Indian Literature, Vol. I, Page 310), and in them are treasured a wealth of geometrical and arithmetical results. They can even be considered as works on Engineering, with definite instructions for building altars for which all knowledge about numbers has been used to advantage, just as in modern times all available Mathematics is made use of in Engineering. The works on Engineering are not expected to give the proof of the Mathematical results or to present the Mathematical rigour, as their aim is simply to make use of the formula and not to expound the methods by which it is obtained, and as such, the value of √2 is given in the form of a formula.

We live amidst a civilisation where Mathematics is highly advanced and thus we run the risk of missing the true import of the early researches and investigations now so familiar to us ; but from the point of view of the history of Mathematics, these early results are but the first milestones in the progress of the science and they help the historian to place on record the gratitude of mankind to the *real* originators of the science.

The value of √2 is given in the following Sutra or the formula—

करणी तृतीयेन वर्धयेत्तच्च स्वचतुर्थेनात्मचतुस्त्रिंशोनेन सविशेष: ।

Translation :—Increase the measure by its third part and this third by its own fourth less the thirtyfourth of that fourth, is Saviśesha, or √2.

When expressed mathematically

$$\sqrt{2} = 1 + \frac{1}{3} + \frac{1}{3.4} - \frac{1}{3.4.34}.$$

This value of √2, when worked out, is found to be correct to five places of decimals. The question is how is it arrived at ? The explanation given by Prof. Thibaut (Asiatic Journal of Bengal, Vol. XLIV, 1875), as to the probable calculations the Sutrakaras might have done, fails to give us the reasons for the presence of all the factors in the fractions, in the value of √2 except the factor 34.

He thinks that they must have taken squares of sides 1, 2, 3 ... etc. up to 20 units and written down the squares of their diagonals and compared them with the nearest square number. He thus gives a table:

Side of the square	Square of the diagonal	Nearest Sq. No.
1	2	1 (= 1^2)
2	8	9 (= 3^2)
...	...	...
5	50	49 (= 7^2)
...	...	...
12	288	289 (= 17^2)

He thus chooses the three cases in which the number expressing the square of the diagonal differs by one from a square number. The cases are 8—9, 50—49, 288—289, the last case being the most favourable as it involves a largest number. The diagonal of a square the side of which is equal to 12 is very little shorter than 17 as $\sqrt{289}=17$. That is how the factor $17[=\frac{1}{2}\times 34]$ comes in. This explanation seems to have been suggested to Thibaut from an example given by a commentator of a later date which gives

$$16\frac{33}{34} = 12 + \frac{12}{3} + \frac{12}{3 \cdot 4} - \frac{12}{3 \cdot 4 \cdot 34}.$$

But this is indeed a case, recommended itself by being first in which the third part of a number and the fourth part of the third part are both integral numbers. Thus his explanation fails to satisfy us. G R. Kaye states (Indian Mathematics by Kaye) that "given a scale of measure based upon the change ratio 3, 4 and 34 (since they had a scale 34 *tilas* = 1 *anguli*) the result is only an expression of direct measurement." In my opinion Mr. Kaye has put the cart before the horse Even accepting such an erroneous statement, the question still remains, why did they choose such a scale or what led them to have such a scale of units ? Prof. Thibaut observes : "Nothing in the Sutras would justify the assumption *that they were expert in long calculations," and Kaye conveniently quotes only these words of Thibaut to qualify his statement and purposely avoids a further statement by Thibaut which is not only an answer to Kaye, but Thibaut thereby refutes his own statement. For he further says, "As the diagonal of a square is in reality an incommensurable quantity we can expect an approximate value but their approximation is *remarkably closed one*." No doubt in Sutras they did not try to exhibit their expertness in long calculations,but it must be noted,that Śulvasutras are not mathematical works but works that had their origin in religious duties performed and, as such, there was no need of parading the above mentioned quality. They gave the value of $\sqrt{2}$ correct to five places of decimals, and in those days it was really an uncommon achievement. How did the scale 34 *tilas* = 1 *anguli* and 12 *angulis* = 1 *prādesh* came into existence ? Out of all the numbers, why the number 34 was suggested to Baudhāyan—the author of the oldest Śulvasutra—to define the measure *anguli* instead of any round figure ? It is in fact, Baudhāyan came, in the calculations

of $\sqrt{2}$, across the 34th part of $\frac{1}{17}$ that led him to introduce this scale of relation. Baudhayan adopted the system of units befitting the scientific mind that harnesses theory with practice. For instance, why is the metric system of units introduced ? because it facilitates calculations in scientific experiments. The same genius that introduced the metric system was present in Baudhayan when he used the value of $\sqrt{2}$ in defining his units and their measures. This is therefore the first attempt on the part of Baudhayan to make the theory suit the practice and full credit must go to him for its priority.

It appears to my mind that this value of $\sqrt{2}$ must have been arrived at by the method of approximations where the quantities of higher order of smallness are neglected or by the method which wrongly goes under the name Tannery's R-process.

In this connection the reader must first of all note down an earlier Sutra.

अध्यर्धं पुरुषा रज्जुर्द्वौ सपादौ करोति

Translation :—A cord of the length of one and a half *purusha* makes two and a quarter square *purushas*.

This shows that the Sutrakaras knew that the area of the square whose side $(1+\frac{1}{2})$ units is $2\frac{1}{4}$ square units, *i.e.*,

$$(1+\tfrac{1}{2})^2 = 2\tfrac{1}{4} > 2.$$

Hence they tried the square of $(1+\frac{1}{3})$

But $(1+\tfrac{1}{3})^2 = \dfrac{16}{9} < 2$

$$2 - \dfrac{16}{9} = \dfrac{2}{9}.$$

So they further took the quantity x, so that

$$(1+\tfrac{1}{3}+x)^2 = \dfrac{16}{9} + \dfrac{8x}{3} + x^2.$$

x^2 they omitted as the quantity of higher order of smallness. Hence putting

$$\dfrac{8x}{3} = \dfrac{2}{9}, \qquad \text{we have}$$

$$x = \dfrac{1}{12} = \dfrac{1}{3.4}$$

$$\therefore \sqrt{2} = 1 + \dfrac{1}{3} + \dfrac{1}{3.4} \quad \text{as the second approximation.}$$

Further $\left(1+\dfrac{1}{3}+\dfrac{1}{3.4}\right)^2 = \left(\dfrac{17}{12}\right)^2 = \dfrac{289}{144} > 2$

$$2 - \dfrac{289}{144} = -\dfrac{1}{144}.$$

So they further took the quantity y (say) such that

$$\left(1+\frac{1}{3}+\frac{1}{3\cdot4}+y\right)^2=\frac{289}{144}+\frac{34y}{12}+y^2.$$

y^2 they omitted, and hence putting

$$\frac{34\,y}{12}=\quad-\frac{1}{144}\text{, we have}$$

$$y=\frac{1}{3\cdot4\cdot34}$$

$$\therefore\quad\sqrt{2}=1+\frac{1}{3}+\frac{1}{3\cdot4}-\frac{1}{3\cdot4\cdot34}$$

Or they might have followed another method that consists of splitting the quantity under the radical sign into two parts—one complete square and the other the remaining part, *i.e.*, the method that gives

$$\sqrt{A^2+b}=A+\frac{b}{2A}\quad\text{approximately.}$$

Thus

$$\sqrt{2}=\sqrt{1+1}=1+\tfrac{1}{2}\text{, as the first approximation.}$$

But they knew that

$$\left(1+\frac{1}{2}\right)^2=\left(\frac{3}{2}\right)^2=\frac{9}{4}>2.$$

$$\therefore\quad\text{They tried}\quad\left(1+\frac{1}{3}\right)^2=\left(\frac{4}{3}\right)^2=\frac{16}{9}.$$

$$\text{But}\quad\frac{16}{9}<2\;by\;\frac{2}{9}.$$

$$\therefore\;\sqrt{2}=\sqrt{\frac{16}{9}+\frac{2}{9}}=\sqrt{\left(\frac{4}{3}\right)^2+\frac{2}{9}}$$

$$=\frac{4}{3}+\frac{\left(\frac{2}{9}\right)}{2\cdot\left(\frac{4}{3}\right)}=\frac{4}{3}+\frac{1}{3\;4}$$

$$=1+\frac{1}{3}+\frac{1}{3.4}\text{, as the second approximation,}$$

$$=\frac{17}{12}$$

$$\text{And}\left(\frac{17}{12}\right)^2=\frac{289}{144}$$

$$\text{But}\;\frac{289}{144}<2\;by\;\frac{1}{144}$$

$$\therefore \sqrt{2} = \sqrt{\frac{289}{144} - \frac{1}{144}} = \sqrt{\left(\frac{17}{12}\right)^2 - \frac{1}{144}}$$

$$= \frac{17}{12} - \frac{\left(\frac{1}{144}\right)}{2 \times \left(\frac{17}{12}\right)} = \frac{17}{12} - \frac{1}{3.4.34}$$

$$= 1 + \frac{1}{3} + \frac{1}{3.4} - \frac{1}{3.4.34}$$

and so on.

Had they required the further approximations, they would have proceeded in the same manner but they did not find it necessary, as this value of "Saviśesha," *i.e.*, $\sqrt{2}$, served their purpose quite all right.

The second method is but a little variation of the first but it must have been this very method by which the Sutrakaras obtained the value of $\sqrt{2}$ as it is in conformity with the word Saviśesha (सविशेष):

सविशेष = स + वि + शेष

शेष—means remainder or anything left out to be said;

वि—as a prefix to nouns not immediately connected with roots expresses negative sense and hence विशेष means without anything being left out to be said, *i e*, complete in itself—*i e.*, a complete square;

स—the prefix attached to nouns means 'the same'—'the celebrated'
. —'the distinguished '

Hence सविशेष means the distinguished or the celebrated complete result.

विशेषित: शेष: तेन युक्तं—सविशेषितशेष: or सविशेषशेष: or for brevity सविशेष:

Thus in $\sqrt{2}$,

$1, \dfrac{16}{9}, \dfrac{289}{144}$ are the विशेष with $1, \dfrac{2}{9}, -\dfrac{1}{144}$ as the corresponding शेष.

For example in $\sqrt{41}$ *i.e.* $\sqrt{36+5}$

36 is विशेष and 5 is शेष.

Thus it is evident that the process

$$\left[\sqrt{A^2 + b} \longrightarrow \left(A + \frac{b}{2A} \right) \right]$$

must be known, because of its priority, as the Saviśesha process and not as Tannery's R process. Saviśesha process is at least as old as 750 B.C., and bears a strong testimony that the Hindus had made enormous strides in the science of Mathematics in ancient days.

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　　　Poona.

THE PROBLEM OF SQUARING THE CIRCLE AS SOLVED IN THE ŚULVASUTRAS

By

PROFESSOR L. V. GURJAR, M.A.

SQUARING the circle is one of the celebrated problems that have attracted the attention of the great thinkers of the world for centuries together. It means simply the problem of the quadrature of the circle, and endeavours towards its solution have been made from time to time, until Lindemann (Ber. Akad. Berlin, 1882) established the transcendence of the value of π which finally decided the fact that the quadrature or the rectification of a circle whose diameter is given is impossible by a construction in which the use only of algebraic curves is allowed.

In Europe till the invention of the Differential and the Integral Calculus in the middle of the 17th century, the main activity of the mighty thinkers, from Archimedes (287—212 B.C.) to Huyghens (1629—1665), towards the solution of this problem, consisted in the approximate determination of π by calculations of the sides or areas of regular polygons inscribed or circumscribed to the circle. Such attempts were made in India as well, since the dawn of the Vedic civilisation to the end of the 12th century. In the Vedic age it was a problem which had its origin in the religious rites performed—*i.e.*, of constructing the circular altar equal in area to a square and *vice versa*. Though the value of π (=3.088) they obtained, is very approximate, still we have to consider it from the point of view of the history of Mathematics. This value of π is found in Śulvasutras—the works that are composed during the period 1500—750 B.C. according to the general estimate of Winternitz (History of Indian Literature, Vol. I, page 310), and we can overlook the error regarding the decimal figures, as it is the earliest determination of the value of π.

The object of the present article is to state the rules by which the ancient Hindus tackled this problem and to place before the reader the probable calculations they might have done in establishing the result.

The problem of finding the circle equal in area to the square has been given first.

Baudhayan Śulvasutra states :

चतुरस्रं मण्डलं चिकीर्षभक्षणार्धं मध्यात्प्राचीमभ्यापात-
येद्यदतिशिष्यते तस्य सह तृतीयेन मण्डलं परिलिखेत्।

Translation :—If you wish to turn a square into a circle stretch a cord of the centre (of the square) towards one of the corners, draw it round the side and describe a circle together with the third part of the piece standing over.

To express it properly :
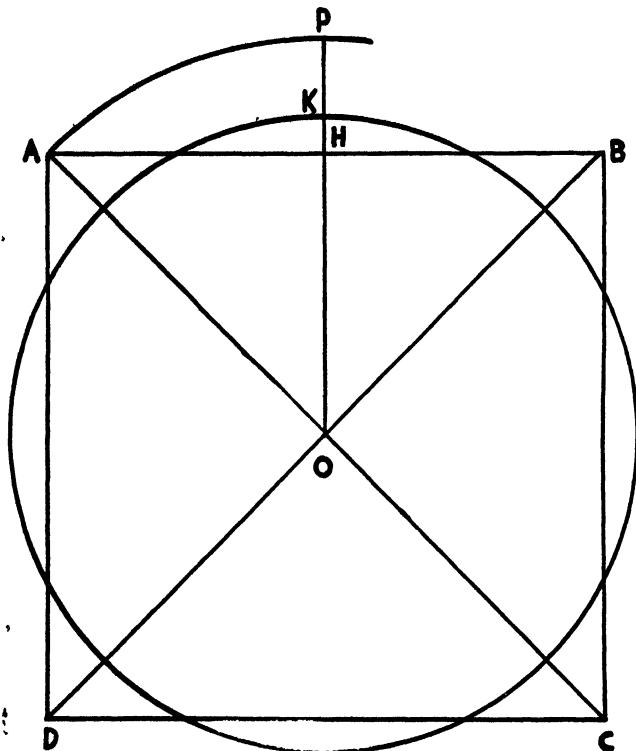
Let ABCD be a square with centre O. Turn OA till it assumes the position OP⊥ to AB, cutting AB in H. Take HK in HP equal to⅓HP. Then with OK as radius, describe a circle which will be equal in area to the square.

Let us examine the value of π given by this construction. Let a be the side of the square.

Then OA = ¼ the diagonal of the square

$$= \frac{a\sqrt{2}}{2} = \frac{a}{\sqrt{2}}$$

$$\therefore \ \text{OK} = \frac{a}{2} + \tfrac{1}{3}\left(\frac{a}{\sqrt{2}} - \frac{a}{2} \right)$$

$$\therefore 2\text{OK} = \frac{a}{}\left(2 + \sqrt{2} \right)$$

$$\therefore \ d \ = \frac{a}{3}\, (2 + \sqrt{2}\,), \text{ where } d \text{ is the diameter of the O,}$$

$$\therefore \ \frac{a}{d} = \frac{3(2 - \sqrt{2}\,)}{2} \quad .. \quad — \quad — \quad — \quad \text{I}$$

Now $\dfrac{\pi d^2}{4} = a^2$ gives

$$\frac{a}{d} = \frac{\sqrt{\pi}}{2}$$

$$\therefore \quad \frac{\sqrt{\pi}}{2} = \frac{3}{2}\left(2 - \sqrt{2}\right)$$

$$\therefore \quad \sqrt{\pi} = 3\left[2 - \left(1 + \tfrac{1}{3} + \frac{1}{3.4} + \frac{1}{3.4.34}\right)\right]$$

$$\left(\because \quad \sqrt{2} = 1 + \tfrac{1}{3} + \frac{1}{3.4} - \frac{1}{3.4.34}\right)$$

$$\therefore \quad \sqrt{\pi} = \frac{3 \times 239}{12 \times 34}$$

$$\therefore \quad \pi = \frac{51489}{166464}$$

$$= 3 \cdot 088$$

Curiously enough, when the converse problem has been stated, the value of π, when worked out, turns out to be exactly the same. For, the converse has been stated as :

मण्डलं चतुरस्रं चिकीर्षन्विष्कंभमष्टौ भागान्कृत्वा भागमेकोनत्रिंशधा विभज्याष्टविंशति भागानुद्धरेद्भागस्य च षष्ठमष्टमागोनम् ।

*Translation :—*If you wish to turn a circle into a square, divide the diameter into eight equal parts, and again one of those parts into twenty-nine parts ; of these twenty-nine parts and the sixth part of the one left part less, with the eighth part of the sixth part.

Thus if a be the side of the square and d be the diameter of the circle,

$$a = d\left[1 - \frac{1}{8} + \frac{1}{8.29} - \frac{1}{8.29.6} + \frac{1}{8.29.6.8}\right] \quad\text{——(II)}$$

Here again—

$$\frac{\pi d^2}{4} = a^2 \quad \text{gives}$$

$$\frac{\sqrt{\pi}}{2} = \frac{a}{d} = \left(1 - \frac{1}{8} + \frac{1}{8.29} - \frac{1}{8.29.6} + \frac{1}{8.29.6.8}\right)$$

$$\therefore \quad \sqrt{\pi} = \frac{9785}{5568}$$

$$\therefore \quad \pi = \frac{95746225}{31002624}$$

$$= 3.088$$

There is much speculation as to the method Baudhayan might have employed in establishing the relation II between a and d. Prof. Thibaut tries to give an explanation that is based upon the work of a commentator of a later date (Asiatic Journal of Bengal, 1875). His explanation is as follows :

"Baudhayan assumed $a = 24$ *angulis*, $\therefore \frac{a}{2} = 408$ *tilas* (as 34 *tilas* = 1 *anguli*). Hence half the diagonal of the square

$$\frac{a}{\sqrt{2}} = 12\sqrt{2} = 12\left(1 + \tfrac{1}{3} + \frac{1}{3.4} - \frac{1}{3.4.34}\right)$$

$$= 16\,\tfrac{13}{34} = 16 \text{ } angulis \text{ and } 33 \text{ } tilas$$

$$\therefore \quad \frac{a}{\sqrt{2}} - \frac{a}{\sqrt{2}} = 4 \text{ } angulis \text{ and } 38 \text{ } tilas = 169 \text{ } tilas$$

$$\therefore \quad \tfrac{1}{3}\left(\frac{a}{\sqrt{2}} - \frac{a}{2}\right) = 56\tfrac{1}{3} \text{ } tilas$$

The radius of the circle $= a + \tfrac{1}{3}\left(\frac{a}{\sqrt{2}} - \frac{a}{2}\right)$

$$= 408 + 56\,\tfrac{1}{3}$$
$$= 464\,\tfrac{1}{3} \text{ } tilas$$

"In other words if half the side of the square is 408 *tilas* long, the length of the radius of the circle amounts to $464\tfrac{1}{3}$ *tilas*. In order to avoid the fraction, both the numbers were turned into thirds, the radius made $= 1393$, and half the side $= 1224$. Finally, the diameter was taken instead of the radius and the whole side of the square instead of half the side.

"To generalise this rule, it was requisite to express 1224 in terms of 1393 One eighth of 1393 is equal to $174\tfrac{1}{8}$, this multiplied by 7 is equal to $1218\tfrac{7}{8}$. Difference between $1218\tfrac{7}{8}$ and 1224 is $5\tfrac{1}{8}$. Dividing 174 (Baudhayan takes 174 instead of $174\tfrac{1}{8}$, neglecting the fraction as either insignificant or more likely as inconvenient) by 29 we get 6. Subtracting from 6 its sixth part, we get 5 and adding to this the eighth part of this sixth part, we get $5\tfrac{1}{8}$.

In other words

$$1224 = 1392\left(\frac{7}{8} + \frac{1}{8.29} - \frac{1}{8.29.6} + \frac{1}{8.29.6.8}\right)$$

Due allowance is being made for the neglected $\tfrac{1}{8}$".

To my mind it appears that this is not the method by which Baudhayan might have arrived at such a wonderfully accurate result in consideration of the same value of π in both the cases.

The logical interpretation must have been as follows :

There is no need to take a square whose side is 24 *angulis*.

For,

$$d = \frac{a}{3}\left(2 + \sqrt{2}\right)$$

$$\therefore \frac{d}{a} = \frac{1}{3}\left[\,2 + 1 + \frac{1}{3} + \frac{1}{3.4} - \frac{1}{3.4.34}\,\right] = \frac{1393}{1224}$$

$$\therefore \frac{a}{d} = \frac{1224}{1393}$$

To generalise this rule it was essential to express 1224 in terms of 1393. So while working it out, Baudhayan found the greatest possible integral number that would divide both the numerator and the denominator giving small remainders. To obtain this number, divide 1393 by 1224, and the remainder is 169, the possible common measure for the two numbers 1393 and 1224. If 1393 is divided by 169, the quotient is 8 and the remainder is 41 : while if 1224 is divided by 169, the quotient is 7 and the remainder is 41. In the first case, to reduce the remainder to its lowest value by keeping quotient 8, and in the second case to reduce the remainder to its lowest value by keeping the quotient 7, the greatest common measure would be 174, since $174 \times 8 = 1392$, and thus the remainder left is 1, and $174 \times 7 = 1218$, and leaves the remainder 6. Thus after 169, Baudhayan must have by turn divided both the numbers by 170, 171, 172, 173 and 174, and stopped at 174, since it served the required purpose. This process involves simple division and therefore it is easily suggestible. Thus Baudhayan obtained the maximum divisor for minimum remainders, since the idea was simply to express 1224 in terms of 1393. Thus—

$$\frac{a}{d} = \frac{1224}{1393} = \frac{\left(\frac{1224}{174}\right)}{\left(\frac{1393}{174}\right)} = \frac{\left(7 + \frac{6}{174}\right)}{\left(8 + \frac{1}{174}\right)} = \frac{7 + \frac{1}{29}}{8 + \frac{1}{6.29}}$$

$$= \frac{\left(\frac{7}{8} + \frac{1}{8.29}\right)}{1 + \frac{1}{6.8.29}} = \left(7 + \frac{1}{8.29}\right) \cdot \frac{1}{\left(1 + \frac{1}{68.29}\right)}$$

$$= \left(1 - \frac{1}{8} + \frac{1}{8.29}\right) \times \frac{1}{1 + \frac{1}{6.8.29}}$$

Now the value of the factor $\left[\dfrac{1}{\left(1 + \dfrac{1}{6.8.29}\right)}\right]$ is obtained by simple

division just as

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \ldots \ldots \ldots$$

can be obtained by simple division.

$$\therefore \frac{1}{1 + \frac{1}{6.8.29}} = 1 - \frac{1}{6.8.29} + \left(\frac{1}{6.8.29}\right)^2 - \left(\frac{1}{6.8.29}\right)^3 + \ldots$$

$$\therefore \frac{a}{d} = \left(1 - \frac{1}{8} + \frac{1}{8.29}\right)\left(1 - \frac{1}{6.8.29} + \ldots - \right)$$

higher powers in the second bracket being neglected as they are small.

$$\therefore \frac{a}{d} = 1 - \frac{1}{8} + \frac{1}{8.29} - \frac{1}{6.29.8} + \frac{1}{8.29.6.8} - \frac{1}{8.29.6.29.8}$$

Omitting the last term as it is small, we have

$$\frac{a}{d} = 1 - \frac{1}{8} + \frac{1}{8.29} - \frac{1}{6.29.8} + \frac{1}{8.29.6.8}$$

So it would be observed that by making use of simple division, the Sutrakaras made use of the Binomial theorem with the negative unit index, and they were perfectly justified in doing so as the argument x is less than unity. Throughout, this process is based upon ordinary division and as such it is easily suggestible.

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        Poona.

STUDIES IN EDUCATIONAL STATISTICS: 0 (INTRODUCTION)

EXAMINATION STANDARDS IN INDIA

By

R. P. SHINTRE

EXAMINATIONS form a very important element in the Indian system of education. There are examinations at the entrance of the secondary as well as of higher or University education. There are examinations for admission to different technical courses ; there are examinations for recruitment to most of the Government services and there are departmental examinations after recruitment also. In fact for a person of our new but rapidly growing middle class, it is impossible to get any job without passing one or more examinations. Examinations may, therefore, be considered as influencing the whole colonial-bourgeois social system of our country. The problems of examinations are many and varied, as they touch educational and social life at so many points. They may, however, be visualised as those related mainly to fixing the purpose of an examination and those of setting up an efficient mechanism for carrying it out.

It is not intended to give here any exhaustive bibliography of books on, or references to work regarding, examination statistics ; because they have no bearing on the problem as it is viewed here. The books[1] I have seen may be classified as under :—(i) the Edgeworth type represented by the works of Hartog and his collaborators ; in these books, the vagaries of examiners and the deficiencies of the mechanism are discussed but without an effective remedy for the ill, unless perhaps the examination system itself be abolished ; (ii) books which attempt to discuss both distribution and effectiveness primarily with a view to suggest changes mainly for greater efficiency, fairness and uniformity between various subjects; (iii) the Government report type which give the examination 'statistics' as the economists understand the term; for, they only give a mass of tabulated data without regard to its usefulness to the statistician.

Books of type (iii) may be here ignored as the data they give are rarely fit for an application of modern statistical technique. Books of types (i) and (ii) usually obtained in our libraries have one striking defect in common, viz., the absence of the application of any test of significance or even the knowledge of such tests. For example, the table on page 3 and that on page 9 of 'The Marks of Examiners' by Hartog, Rhodes and Burt give an impressive illustration of the vagaries of examiners as demonstrated by the marks allotted by the same fourteen[*] examiners to

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[*] As examiner A in the table on page 3 does not appear in the table on page 9, his marks are not considered.

the same fifteen scripts at an interval of one year. This, at the time of publication, must have made a sensation among the mentally awake school-masters. But the able and well-meaning writers could go no further than to suggest some idealisations in place of effective remedies. A modern statistician would immediately work out the following analysis of variance from the data of these tables.

Analysis of Variance

	D.F.	S.S.	M S.	F.
Blocks ..	1	546.29	546.29	2.86
Students ..	14	15829.44	1130.67	59.16***
Examiners .	13	8568.54	659.12	34.49***
B. × S. ..	14	645.03	46.07	2.41**
B. × E. ..	13	994.68	76.51	4.00***
S. × E.	182	. 9466.49	52.01	2.72**
B. × S. × E. ..	182	5479.50	19.11	s.d. = 4.37
Total..	419	39528.97		

In spite of the fact that there is a great variation in the marks assigned to some students by some examiners there is no significant difference in the markings of the two blocks. Although there is significantly great variation both between the students and the examiners, the difference between the students is considerably greater than that between the examiners ; and this is what is usually required in an examination. As a method of discrimination, the mechanism shows a standard error per entry of 4.37 marks based on the residual mean square in the analysis. So a difference of $8.74/\sqrt{14}=2.34$ marks from the average marks obtained from all fourteen examiners is not to be expected oftener than once in twenty candidates in this rather ill-designed* experiment. A statistician would also realise the futility of any attempt at discrimination that went deeper than this. No statistician can say anything about the justice or injustice of *any given single entry*.

Among the books of type (*u*) is 'Secondary School Examination Statistics' by Crofts and Jones, in which we notice on page 57 the statement :

"The percentages of boys and girls gaining a certificate were—

	1923	1924	1925	1926	1927
Boys ..	69.8	63.9	66.2	66.2	66.0
Girls ..	71.3	65.6	66.4	66.4	67.1

"The percentage of girls gaining a certificate is higher than that of boys in each of these five years ; but the difference is not large and *it may not be significant* of any real difference between them in ability, training

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* A few remarks by the very able reviewer (F.S.) of this book may be quoted. 'It seems most unlikely that the experiment was devised by any one who had any knowledge of the work of Fisher on the design of experiments.'.....'We may regret that the investigations used such very small samples.'....'The report of all this work is, therefore, unsatisfactory in many ways, both in the matter of procedure and of presentation'. See pp. 10.-10 of 'Journal of the Royal Statistical Society,' Vol. 100 (1937), part 1.

or any other factors which make for success, in examination." (Italics are mine.)

But the following analysis of variance or the value of t (2.9636) for the t test would show that the difference is significant at about the 2% level, considering that the difference is always in the same direction.

	D.F.	S.S.	M.S.	F.
Sex ..	1	2.209	2.209	8.78
Years ..	4	37.574	9.3935	37.35
Residual ..	4	1.006	0.2515	s.d.=0.5015
Total..	9	40.789		

The chi-square test could also be made to give significant results if the actual numbers (and not the percentages only) of the boys and girls were given.

It is also unfortunate that books of this type are marred by the most thoroughly outmoded of Pearsonian Statistics such as Spearman's rank correlation* coefficient of which the significance and the mathematical basis were not properly settled until a comparatively recent date.

For the Indian examinations, none of these types of books can be said to exist on a considerable scale, though small beginnings have been made. In this connection may be pointed out the work (published in Sankhya) done by P. C. Mahalanobis and his collaborators ; J. B. Hutchinson and B. M. Pugh have also published in 'Annals of Eugenics,' Vol. VIII, 'A Note on the Importance of Differences between Examiners.'

The special applicability of statistical methods to Indian examinations, as distinct from examinations in England or America (I have little information about examinations in other countries), lies in the fact that in India exact numerical marks are given for all subjects in most examinations; and the average pass mark is rather low, even as low as 30% as against 60% in the United States of America. In India the higher instruction is given and examinations are mostly held in a language foreign to virtually all candidates ; and finally, these examinations have a special importance and an unusual stiffness ; for they are intended to create a hierarchy of examinations oriented towards Government service. There is one essential difference between the examinations conducted by the Universities and those by the Government. The economic necessity and public opinion appear to have tended in recent years to relax the University standards. [At least this is the general impression and the statistician must take necessary steps either to prove or disprove it.] But no such claim can be made for Government examinations in which the percentage of candidates selected from the applicants (examinees) has steadily decreased due to the enormous increase in the number of applicants for each post advertised vacant. The function of the Universities in India has still remained what it was, viz., to furnish the candidate with the hall-mark of ability or 'fitness' of some sort. The Government examinations, which give to the candidates the most desired prizes (well paid Government services), retain their original purpose of weeding out all but a very small number.

* See the article of Harold Hotelling and Margaret Richards Pabst, 'Annals of Mathematical Statistics,' Vol. VII, No. 1 of March 1936, pp. 29-43.

The Indian Universities have only very recently and barely begun to realise that their curricula must be framed not on the style of the Cambridge Tripos or the Oxford Greats of the last century nor the current I.C.S. schedule but that the curricula should suit the needs of the newly developing middle class (usually heralded as 'National') economy. So that there is now at least a talk in our Universities of adjusting their studies to suit the requirement of the average boy in his after life, not realising however, that the 'average boy' is a meaningless abstraction without a statistical study of the students as also of the needs of their 'after life.' The original ecclesiastical functions of the European Universities never existed in India nor did their more recent function in Britain of breeding a special ruling class of 'gentlemen.' On the other hand the Government services examinations, as far as one can see, have no visible connection between the subjects of any examination and the service for which the examination selects candidates ; the only argument in favour of such an arrangement being that the examination tests the general ability of the candidate who, if selected, can receive the necessary departmental training afterwards. In view of the great influence of examinations for Government service on our educational system, it is worth pointing out that the above argument is fallacious. Far better services could be secured, without the necessity for the candidate to have to undergo some sort of University training, by requiring the candidate to submit to an examination in a specialised technical syllabus to suit the requirement of the service concerned. It may also be borne in mind that recruitment for many of the services is made also by selection and not entirely by examination ; and these services are not known to be particularly inefficient by current Indian standards. The fact is that the lower clerical staff normally does all the work and the politician determines the policy ; so that the higher staff selected by the examination has little original work to do.

These extraneous matters, not to be discovered by a mere statistical analysis, nevertheless have a great influence on examinations of Indian Universities. The statistician should not try to adjust the examinations to some abstract standard of his own, but he should first gather and analyse all available information regarding examinations.

When we regard any examination we may concentrate upon two points. (i) What is the main object of the examination in its test of ability ? Which ability, if any, of the candidate does it profess to test ? (ii) How efficiently is the testing done ? We can only deal with these questions so far as they are connected with University examinations and even there only to the extent of the available data.

Regarding these points it may be seen that the only ability tested directly by any examination is the ability to score marks in that examination. To what extent this scoring of marks depends upon the vagaries of the examiner has been discussed without a definite conclusion ; whether and how this ability is correlated to other types of ability has yet to be determined, if the question admits of a reasonably satisfactory solution. The methods for testing this are precisely those given by R. A. Fisher in his 'Design of Experiments.' The first point is not a matter within the province of the statistician and must be dealt with by the educationist and the psychologist.

It will be quite relevant to quote here from the Presidential address*
of the outstanding British mathematician, G. H. Hardy, to the London
Mathematical Association. The title of the address was 'The Case
Against the Mathematical Tripos' ; but I shall only quote his remarks
regarding examinations in general.

> "Denunciation of examinations, like denunciation of lectures, is very popular
> now among educational reformers, and I wish to say at once that most of what
> they say, on the one topic and on the other, appears to me to be little better
> than nonsense.... There are in fact certain traditional purposes of exam-
> inations, purposes for which they always have been used and for which they
> seem to me to be the obvious and appropriate instrument. There are certain
> qualities of mind which it is often necessary to test, and which can be tested by
> examinations much more simply and more effectively than in any other way.
> If a teacher wishes to test his pupils' industry, for example, or their capacity
> to understand something he has told them, something perhaps of no high order
> of difficulty, but difficult enough to require some little real intelligence and
> patience for its appreciation, it seems to me that his most reasonable course is
> to subject them to some sort of examination. Examinations have been used
> in this manner from time immemorial, in every civilised country ;.... and
> with such examinations I have no sort of quarrel..... I said that under certain
> conditions I believed in examinations, that is to say in examinations of a
> sufficiently lowly type, which do not profess to be more than a reasonable test
> of certain rather humdrum qualities. The phrases which I used were vague,
> and I ought no doubt to attempt to define my own standard a little more
> precisely. This is naturally not quite easy but I will risk some sort of definition.
> I should say, roughly, that the qualities which I have in mind—reasonable
> industry, reasonable intelligence, reasonable grasp—would be about sufficient
> to carry a candidate, in any of the orthodox Oxford or Cambridge examinations,
> into a decent second class. Beyond that I do not believe in recognising differ-
> ences of ability by examination.... 'What,' he [Mr. Justice Romer] asked
> judicially, 'is the function of the Tripos ?' and he replied, 'Surely to examine
> and to make distinctions between young men ' It would indeed be difficult
> to compress a larger quantity of vicious educational doctrine into a smaller
> number of words The exactly opposite doctrine, that no distinctions should
> be made by examination except such as practical necessities may make im-
> perative, is surely somewhere a little nearer to the truth..... I suppose, in
> fact, that the Universities, and most of the other bodies in whose hands edu-
> cational patronage is vested, have come in practice to very much the same
> conclusion as my own, that examinations are an admirable test of competence
> and industry, but ineffective and erratic as a test of any higher gift. The
> Government stands alone, so far as I know , in attaching a definite money value
> to an examination class, and even the Government stops short of rewarding
> the only mark which could plausibly pretend to be a mark of real distinction....
> I do not want to reform the Tripos, but to destroy it. And if you ask me if the
> Tripos is a peculiar case, or whether what I have said applies to all other high
> grade honours examinations, I can only answer that, so far as I can see, it does.
> .... Indeed I am afraid that my advice to reformers might sound like a series
> of stupid jokes. I should advise them to let down the standard at every
> opportunity ; to give first classes to almost every candidate who applied ; to
> crowd the syllabus with advanced subjects until it was humanly impossible to
> show reasonable knowledge of them under the conditions of the examination
> In this way, in the course of years, they might succeed in corrupting the value
> of the prizes which they have to offer, and in all probability time would do the
> rest."

It remains, therefore, to judge our examinations not by any arbitrary,
extraneous or preconceived standards but on their own merits, i.e.,
whether they are efficient even as they stand. The results,† obtained

on examining a few examinations of the Bombay University, will be set forth here with indications of such other points as have occurred during the work and the possibilities of investigating some more.

The work was started with the consideration of the total marks obtained by candidates at the F. Y.[*] Examination held by the Fergusson College, Poona, over a fairly long period 1913-1937.

The statistical conclusions[2] arrived at by this investigation may be stated thus :

(i) The examination has become progressively easier.

(ii) It is still much too stiff. Only one out of 7679 could score as much as 80% and only 30 scored more than 70% in 24 years.

(iii) The distribution of total marks scored by the students is practically symmetrical but not normal as there is a significant platycurtosis.

Marks: unit=4 per cent.
Fig. 1
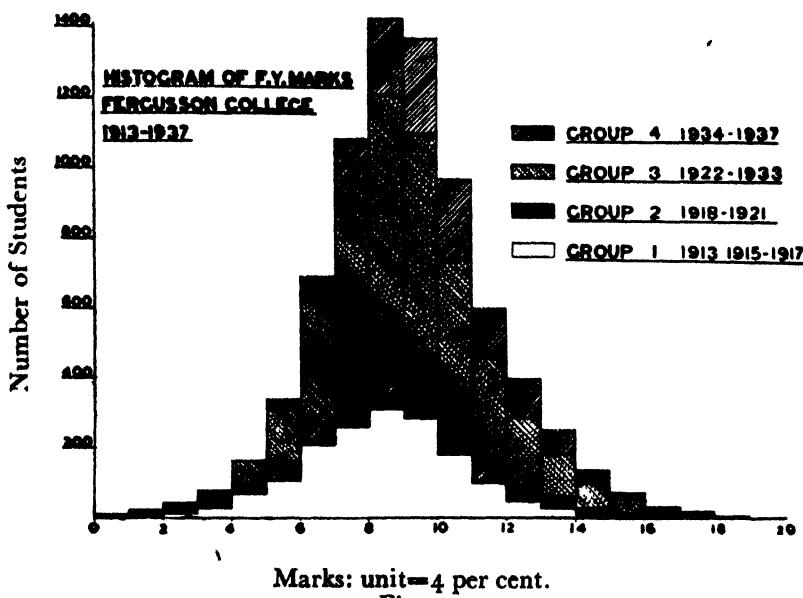
(iv) For three out of four unequal groups into which the period had to be divided, the distribution is of Pearsonian Type VII, and for the remaining group it is of Pearsonian Type IV. This odd type is due to the fact that too many years with a progressively increasing average were inadvertently grouped together. The combined distribution of the whole period is also of Type IV, and for the same reason.

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[*] Between the years 1913-1937, a student passing the Matriculation Examination of the Bombay University (or an equivalent examination) could be admitted to a college affiliated to the Bombay University. At the end of one year the progress of the student was tested by his college by an examination called the First Year Examination in Arts (F. Y. Examination). If the Principal of his college was satisfied about his progress the student was admitted, at his choice, to the Intermediate Arts or Science (I. A. or I. Sc.) class. At the end of this (second) year if he passed the I. A. or I. Sc. Examination held by the University he was admitted to the degree course for Arts or Science. And at the end of two more years he was examined again by the University for the degree of Bachelor of Arts or Science (B. A. or B. Sc.).

The points that may next be considered are (*i*) the nature of the population (matriculates) from which the F. Y. candidates are a sample, (*ii*) the relation of this examination to the next examination, *viz.*, I.A. or I.Sc. held by the Bombay University.

The population of which the F.Y. candidates are a sample must, at the time of admission, be strongly skew-positive with regard to the total marks scored because only those that pass the Matric are admitted to the first year in colleges. It is surprising that this sample in the short period of one year shows a close approach to normality and symmetry with regard to the total marks obtained at the F.Y. Examination. Whether such a study of the F.Y. Examination of other colleges will also lead to the same conclusions is a matter that needs investigation.

A general study of the distribution of Matriculation totals for 1941 shows that the distribution is of Pearsonian Type I, (*i*) skew-negative

Marks.
Fig. 2
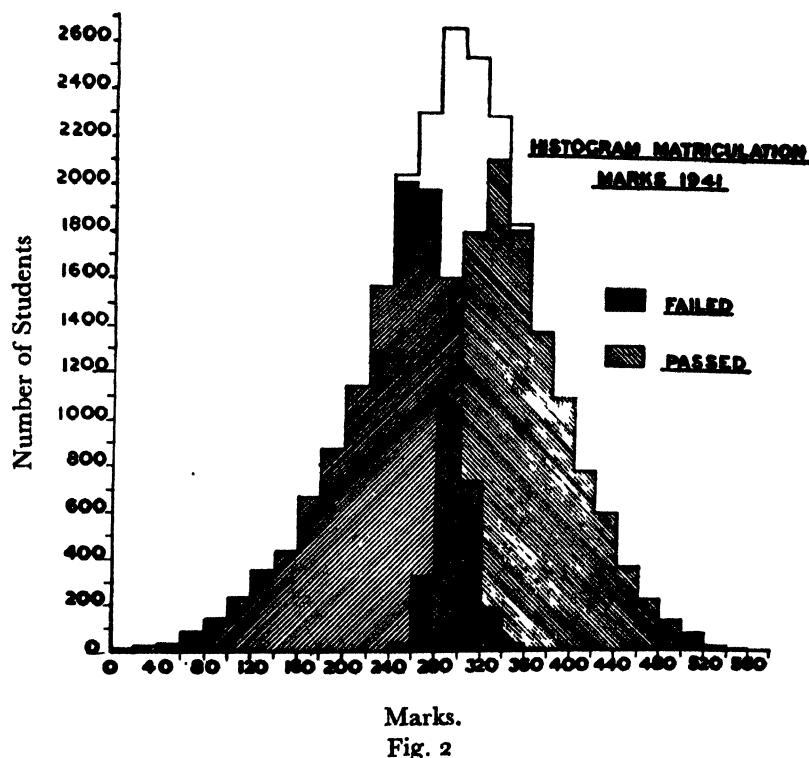
for failed and for all candidates and (*ii*) skew-positive for passed candidates. In the case of all (passed and failed together)-candidates the departure from normality is small but significant. Out of 24145 candidates (taking all papers : non-exemptees) only two scored more than 80% (572 and 578 out of 708) ; so that this examination may also be said to be too stiff, in comparison with the apparatus of instruction. This is the common feature of almost all Indian University examinations, which have all the disagreeable features of a competitive examination without its fruits. A study of these totals can be done in several ways,

i.e., (*i*) by groups, centres or schools ; (*ii*) by age, sex, mother-tongue or caste of the candidates. But work of this kind over several years and the distribution of the sub-sample that enters the colleges every year need closer investigation. Such work is obviously impossible for an individual. It may be done only by the universities themselves or by some associations.

When we say that the examinations are stiff it should not be considered that the remedy lies in the direction of simply allowing more candidates to pass. The economic strain* on the people and the consequent pressure of public opinion will exert their influence in this direction (passing more candidates). But the real remedy will be to ask more questions of an easier nature and if it is feared that this would pass too many candidates the pass mark could be raised.

Proceeding to consider the relation of the F.Y. Examination to the Intermediate Examination of the Fergusson College students†, it was found on the strength of the results of these examinations from 1910 to 1939 that the correlation coefficient r, for percentages of passes for corresponding groups, is .058 which shows that there is practically no relation between the results of the two examinations. This may be due, in the case of the Fergusson College, to the fact that a considerable number of students comes for the Inter to the Fergusson College having taken the F.Y. elsewhere. But for the University as a whole this cannot be the case. This led to the consideration of the results of all colleges affiliated to the Bombay University, taking percentages of passes as the criterion of examination efficiency.

The findings of this* investigation are : (*i*) the B.Sc. has the largest s.d. ; the s.d. is smaller for the arts than for the science examinations ; *i.e.*, the arts examinations are better as examinations than the science examinations ; their results are more consistent and show a higher average. (*ii*) Considering the I.A. Examination against the B.A. and the I.Sc. against the B.Sc. the correlation coefficient is not significant for any college or for all the colleges put together. (*iii*) From the analysis of co variance it is seen that there is a positive significant correlation between colleges eliminating years and a positive but insignificant correlation between years eliminating colleges. There is a negative insignificant correlation for the residual (random) component on the arts side only. (*iv*) Applying Kosambi's test[4] it is found that for both the arts and the science examinations the ratio of generalised variances for colleges to that for years is barely significant at the five per cent. level ; but the variation due to colleges is greater than that due to years. The significance of each, however, against the residual is enormous.

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* In the Matriculation of 1941 of the Bombay University 13373 (49.74%) candidates failed. The cost of educating them for a year at Rs. 52·75 per head (Bombay Education Report, 1939-40) would be Rs. 705425·75. If the extra cost of maintenance, which cannot be considered less than Rs. 100 per head per year, is taken into account, these failures have cost the people over two million rupees. If a small fraction of this amount is spent on analysing the examination in detail, it would help to improve the mechanism and find methods of persuading and preventing the most hopeless candidates from wasting their resources in trying to pass the examination.

† For the consideration of the relation between these examinations in other colleges see 'Studies in Educational Statistics—II,' Fergusson College Magazine, February 1941.

In this investigation the results of colleges were considered on the percentage basis. But percentages of passes is a doubtful criterion of examination efficiency of the colleges. For, suppose that from a college three candidates appeared for an examination and all passed ; from another college 100 appeared for the examination out of which 90 passed. But it will not be easily accepted that the former college is superior to the latter. The results of colleges were, therefore, considered again by taking the numbers passed and appeared from each college as experimental and preliminary plot yields respectively. (See Ex. 46.1 of R. A. Fisher's "Statistical Methods for Research Workers.") This amounts to eliminating the effect of the variation in the numbers appearing for an examination from the result of that examination ; and this makes the method of adjusted plot yields a better criterion of efficiency than the percentage results, as will be seen by reference to the revised[5] ranking list.

Out of this[5] investigation the following points may be noted : (i) in the case of the I.A. Examination the difference in variation between years and between colleges is significant ; but in the case of the I.Sc. the difference in years is actually and significantly greater ; (ii) in the cases of the B.A. and B.Sc., the colleges show a significantly greater variation than the years ; (iii) for arts examinations, the correlation coefficient r shows values which are significant and satisfactory though the value of the residual correlation is rather high ; (iv) for the science examinations the only significant value of r is that for years ; (v) by Kosambi's test,[4] the effects for colleges and years are highly significant for the arts as well as the science examinations ; but the difference at the one per cent. level between colleges and years is significant for the arts but not for the science examinations.

A similar investigation of the examination efficiency of schools, affiliated to the Bombay University, with reference to the Matriculation Examination, is at present being carried out.

The small sampling theory is best applicable to the results of higher University examinations where the numbers appearing are necessarily small on account of specialisation. In this connection the following analyses may be noted.

<div align="center">UNIVERSITY 'A'</div>

<div align="center">*B.A. (Mathematics Honours) 1939*</div>
<div align="center">(The whole table is not given to save space)</div>

Totals of Papers : 805, 981, 973, 1434, 584, 1067.   (5844)

Totals of Students: 267, 377, 314, 308, 290, 141, 279, 191, 238, 161, 361, 264, 263, 186, 278, 289, 152, 204, 145, 263, 284, 186, 198, 205.
<div align="right">(5844)</div>

<div align="center">*Analysis of Variance*</div>

	D.F.	S.S.	M.S.	F.
Students	23	16785.6	729.8	5.58***
Papers	5	16706.6	3341.3	25.57***
Residual	115	15026.6	130.667	s.d.=11.43
Total	143	48519.0	339.29	

This relates to the B.A. (1939) Examination in Mathematics Honours of a University 'A.' The variation between papers (*i.e.*, subjects-examiners) is much greater than that between students. In particular the departures, from the average, of the fourth and the fifth paper are striking. This was brought to the notice of the authorities concerned and the disparity has since been considerably reduced. It may be noted also that the s.d. (11.43) of a single entry is too great, being about 1/3 the pass mark in any paper.

UNIVERSITY 'B'

M. A. (*Mathematics*) *1941*

	Examiner A		Examiner B		Exmr. C	Exmr. D	Exmr E	Exmr. F	Total
	Paper *i*	Paper *vi*	Paper *iii*	Paper *v*	Paper *ii*	Paper *iv*	Paper *vii*	Paper *viii*	
1	54	45	38	58	90	50	65	53	453
2	11	4	28	29	30	45	40	31	218
3	67	50	55	64	69	55	75	55	490
4	33	27	37	37	15	45	30	48	302
5	26	47	43	40	52	22	27	1	258
6	35	35	41	60	55	68	40	46	389
7	42	34	50	58	45	45	53	63	390
8	29	63	40	56	73	61	10	38	400
9	6	4	5	5	5	6	5	9	45
10	28	21	40	31	33	8	10	11	182
Total	331	330	377	447	497	405	385	355	3127

Analysis of Variance

	D F	S.S	M.S.	F
Students ..	9	21419.7625	2379.9736	18.309***
Papers ..	7	2341.6875	334.5268	2.574*
Residual ..	63	8188.9375	129.9831	s.d. =11.40
Total..	79	31950.3875	404.4353	

This relates to the M.A. (1941) Examination in Mathematics of another University 'B.' The variation between students is significantly great and to that extent the examination may be considered an efficient test, in view of the fact that the variation between papers is significant only at the 5 per cent. level. But the s.d. (11.40) is again too large compared to the pass mark (33) in any paper.

UNIVERSITY 'B'

M. A. (*Ancient Indian Culture*) *1941*

	Examiner A		Examiner B		Examiner C		Examiner D		Total
	Paper *i*	Paper *ii*	Paper *iii*	Paper *vi*	Paper *iv*	Paper *vii*	Paper *v*	Paper *viii*	
1	40	35	23	24	29	21	27	30	229
2	42	44	54	32	31	32	54	50	339
3	44	42	30	20	30	36	34	45	281
4	35	49	21	20	27	17	20	33	222
5	45	54	28	32	50	29	40	50	328
Total	206	224	156	128	167	135	175	208	1399

Analysis of Variance

	D.F.	S.S	M.S.	F.
Students ..	4	1468.850	367.2125	7.9749**
Examiners ..	3	1414.875	471.6250	10.2425**
Papers ..	1	2.025	2.0250	0.0440
E. × P. ..	3	320.075	106.6916	2.3171
Total for 8 Papers ..	7	1736.975	248.1392	5.3889**
E. × S. ..	12	624.750	52.0625	1.1307
S. × P. ..	4	109.850	27.4625	0.5964
S. × P. × E. ..	12	552.550	46.0458	s.d.=6.7857
Total ..	39	4492.975	115.2045	

This analysis is of the M.A. (1941) Examination in Ancient Indian Culture of the University 'B'. For this examination the variation between students is significant but that between examiners is even more so. Thus this examination does not appear to be a satisfactory test of discrimination between students, although the s.d. is lower, than for the other two examinations, as compared to the pass mark (33) in any paper.

ʃ In assessing the difference between examiners, we also measure the conjoint difference of the performance between the several different groups of subjects chosen. The difference will be between examiners alone only if it can be proved that the students were capable of demonstrating equal ability, on the whole, for the subject-groups. The difference between papers 'within an examiner' and the interaction, examiner ×paper, are here fictitious, because there is no reason to suppose that the two papers assigned to each examiner have any *a priori* order, or are in any way comparable in the same manner as plots with two different treatments in several blocks. Hence, their non-significance means less than would be the case if, say, the same'two papers had been assessed by the examiners in question, or even if the examiners had set their own papers in each of two pre-assigned subjects common to all.

It will be recognised that for an examination to be a good test of the abilities of candidates the analysis of its results must show a significant difference between students but preferably not between examiners ; the

residual, at the same time, should give a very low standard deviation compared to the pass mark.

If education and examinations are considered as problems in sampling, (i) we may consider the field of knowledge as one population and pupils as another, the interaction between the two being due to teachers, institutions and methods of education ; (ii) in an examination the sampling from the field of knowledge must be efficient and must also be compatible with the representative of the larger sample chosen by the educationists in fixing the syllabus. In addition to this, as the examination is broken up into several smaller samples as for the individual subjects and papers, the abilities tested by the several papers should in general be positively correlated. But this does not cover all the important questions. The material dealt with is human and the problem, for example, of progressive mental fatigue over a long series of papers has not been determined. There is also the element of chance due to the variability (i) of the conditions of the candidates arising from illness or accident and (ii) in the difficulty of the papers set.

Our examining bodies have unrivalled opportunities for studying the technique of examinations. And if our Universities care to improve the mechanism of their examinations, they should get their examinations statistically analysed. This will help the Universities themselves and should not be considered needlessly expensive. For if a University runs a statistical department of its own it will provide excellent opportunities for students for a practical study of statistical methods. In this work the students will have to learn to collect and tabulate the data, to make a choice of units and to work out analyses of variance and problems in curve fitting, estimation, significance, trends, forecasts, etc. Ultimately it is not too much to hope that our examinations may even come to be properly designed as experiments to test the capacity of a variable population even by means of an apparatus that can never be mechanically perfect.

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BISECTOR PLANES OF THE ANGLES BETWEEN TWO GIVEN PLANES

By

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IN discussing the bisector planes of the angles between two given planes it is customary to distinguish them with reference to origin only. Practically no attempt was made with the equations $a_1x+b_1y+c_1z+d_1=0$ and $a_2x+b_2y+c_2z+d_2=0$, to show how the acute and obtuse angle bisectors can be determined. Simple geometrical consideration will show how this can be done easily.

Note.—In what follows, $\sqrt{\text{any expression}}$ is to be taken with a positive sign only.

Suppose the two given planes are $a_1x+b_1y+c_1z+d_1=0$ and $a_2x+b_2y+c_2z+d_2=0$. The bisector planes of the angles between them are

$$\frac{a_1x+b_1y+c_1z+d_1}{\sqrt{a_1{}^2+b_1{}^2+c_1{}^2}} + \frac{a_2x+b_2y+c_2z+d_2}{\sqrt{a_2{}^2+b_2{}^2+c_2{}^2}} = 0 \qquad \text{(A)}$$

i.e. $\lambda_2 (a_1x+b_1y+c_1z+d_1) \mp \lambda_1(a_2x+b_2y+c_2z+d_2)=0$
where

$$\lambda_1 = \sqrt{a_1{}^2+b_1{}^2+c_1{}^2} \text{ and } \lambda_2 = \sqrt{a_2{}^2+b_2{}^2+c_2{}^2}$$

or $x(a_1\lambda_2-a_2\lambda_1)+y(b_1\lambda_2-b_2\lambda_1)+z(c_1\lambda_2-c_2\lambda_1)+d_1\lambda_2$
$-d_2\lambda_1=0$ (B)

and $x(a_1\lambda_2+a_2\lambda_1)+y(b_1\lambda_2+b_2\lambda_1)+z(c_1\lambda_2+c_2\lambda_1)+d_1\lambda_2$
$+d_2\lambda_1=0$ (C)

Now take the plane (B) and one of the given planes, say, $a_1x+b_1y+c_1z+d_1=0$. The angle between them is given by

$$\cos\theta = \frac{a_1(a_1\lambda_2-a_2\lambda_1)+b_1(b_1\lambda_2-b_2\lambda_1)+c_1(c_1\lambda_2-c_2\lambda_1)}{\sqrt{a_1{}^2+b_1{}^2+c_1{}^2}\ \sqrt{(a_1\lambda_2-a_2\lambda_1)^2+(b_1\lambda_2-b_2\lambda_1)^2+(c_1\lambda_2-c_2\lambda_1)^2}}$$

$$- \frac{\lambda_1{}^2\lambda_2 - \lambda_1(a_1a_2 + b_1b_2 + c_1c_2)}{\lambda_1\sqrt{2\lambda_1{}^2\lambda_2{}^2 - 2\lambda_1\lambda_2(a_1a_2 + b_1b_2 + c_1c_2)}}$$

$$= \frac{\lambda_1\lambda_2 - (a_1c_2 + b_1b_2 + c_1c_2)}{\sqrt{2\lambda_1\lambda_2}\ \sqrt{\lambda_1\lambda_2 - (a_1a_2 + b_1b_2 + c_1c_2)}}$$

$$= \sqrt{\frac{\lambda_1\lambda_2 - (a_1a_2 + b_1b_2 + c_1c_2)}{2\lambda_1\lambda_2}}$$

Now if the plane (B) is to bisect the acute angle between the given planes,

then the angle $\theta < \frac{\pi}{4}$, i.e., $\cos\theta > \frac{1}{\sqrt{2}}$

$$\sqrt{\frac{\lambda_1\lambda_2 - (a_1a_2 + b_1b_2 + c_1c_2)}{2\lambda_1\lambda_2}} > \frac{1}{\sqrt{2}}$$

i.e, $\lambda_1\lambda_2 - (c_1c_2 + b_1b_2 + c_1c_2) > \lambda_1\lambda_2$

i.e., $(a_1a_2 + b_1b_2 + c_1c_2) < o$

i.e., $a_1a_2 + b_1b_2 + c_1c_2$ is $-ve$

Thus if $a_1a_2 + b_1b_2 + c_1c_2$ is $-ve$, the bisector (B) or the bisector with the $-ve$ sign in (A) bisects the acute angle and the bisector with the $+ve$ sign bisects the obtuse angle. Also it can be shown that if $a_1a_2 + b_1b_2 + c_1c_2$ is $+ve$, the bisectors with the $+ve$ and $-ve$ signs in (A) bisect the acute and obtuse angles respectively.

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A NOTE ON DIFFERENTIABILITY

By

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SUPPOSE $u = f(x, y)$ where x, y are functions of t;

then $\dfrac{du}{dt} = \dfrac{\partial f}{\partial x}\dfrac{dx}{dt} + \dfrac{\partial f}{\partial y}\dfrac{dy}{dt}$ I

In proving Equation I, all the well known authors on the subject that I have consulted make use of the continuity of $\dfrac{\partial f}{\partial x}$ and $\dfrac{\partial f}{\partial y}$ .e.g. In art. 158 of the 7th edition of his book Prof. G.H. Hardy stresses the fact that $\dfrac{\partial f}{\partial x}, \dfrac{\partial f}{\partial y}$ should be continuous for the validity of Equation I. To illustrate the point he gives the following example :—

$$u = f(x, y) = \frac{2xy(x+y)}{x^2+y^2} \qquad \text{when} \quad x \mp 0, y \mp 0$$

and $f = 0$ when $x = 0$ or $y = 0$

Here $f_x(0, 0) = f_y(0, 0) = 0$ and if we write

$x = y = t$, we get $u = 2t$, $\dfrac{du}{dt} = 2$, but

$\dfrac{\partial f}{\partial x}\dfrac{dx}{dt} + \dfrac{\partial f}{\partial y}\dfrac{dy}{dt} = 0.1 + 0.1 = 0$ and so the Formula I fails.

Further since the continuity of $\dfrac{\partial f}{\partial x}, \dfrac{\partial f}{\partial y}$, is needed in proving Formula I, it is also needed to establish the law of the mean

$$f(x+h, y+k) - f(x, y) = h\frac{\partial f}{\partial x}(x + \theta h, y+\theta k) + k\frac{\partial f}{\partial y}(x+\theta h, y+\theta k)$$

$$0 < \theta < 1$$

..........................II

Can we not relax the conditions for the validity of these two results? I think if we proceed as indicated in the next few paragraphs we have merely to assume the differentiability of $f(x, y)$. Assuming the continuity of the partial derivatives amounts to much more than assuming the differentiability of $f(x, y)$. I will return to this point later.

Let $u = f(x, y)$

Then we say $f(x, y)$ is differentiable at (x, y) if we can throw $f(x+\delta x, y+\delta y) - f(x, y)$ into the form

$$f(x+\delta x, y+\delta y) - f(x, y) = A\,\delta x + B\,\delta y + \varepsilon p$$

where A, B are independent of δx, δy,

$$p = \sqrt{(\delta x)^2 + (\delta y)^2}\ ,\ \text{and}\ \varepsilon \longrightarrow o\quad \text{as}\ p \longrightarrow o$$

Next putting $\delta y = o$ and $\delta x = o$ in succession and proceeding to the limit we show that

$$A = \frac{\partial u}{\partial x}, \quad = \frac{\partial u}{\partial y}\ \text{whenever the function is differentiable.}$$

So when $f(x, y)$ is differentiable at (x, y) we have

$$\delta u = f(x+\delta x, y+\delta y) - f(x, y) = \frac{\partial u}{\partial x}\delta x + \frac{\partial u}{\partial y}\delta y + \varepsilon\sqrt{(\delta x)^2 + (\delta y)^2}$$

$$\text{where}\ \varepsilon \longrightarrow o\ \text{as}\ \sqrt{(\delta x)^2 + (\delta y)^2} \longrightarrow o \qquad \text{...........III}$$

Now suppose x, y are differentiable functions of a third variable t (so that $\frac{dx}{dt}, \frac{dy}{dt}$ exist and are finite). We divide both sides of III by δt and get

$$\frac{\delta u}{\delta t} = \frac{\partial u}{\partial x}\ \frac{\delta x}{\delta t} + \frac{\partial u}{\partial y}\cdot\frac{\delta y}{\delta t} + \varepsilon\sqrt{\left(\frac{\delta x}{\delta t}\right)^2 + \left(\frac{\delta y}{\delta t}\right)^2}$$

proceeding to the limit and observing that as $\delta t \longrightarrow o$, δx, $\delta y \longrightarrow o$ and $\therefore \varepsilon \longrightarrow o$ (while $\frac{dx}{dt}, \frac{dy}{dt}$ are finite) we get

$$\frac{du}{dt} = \frac{\partial u}{\partial x}\cdot\frac{dx}{dt} + \frac{\partial u}{\partial y}\frac{dy}{dt} \qquad \text{.........................IV}$$

In the course of this proof the continuity of $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$ is not needed. All that we assume is that $f(x, y)$ should be a differentiable function of $(x, y.)$

In the example, quoted by Prof. Hardy, we easily see that the function is not differentiable at the origin. For we must have

$$\frac{2hk\ (h+k)}{h^2+k^2} = o.h+o.k+\varepsilon\sqrt{h^2+k^2}$$

$$\therefore\ \varepsilon = \frac{2\ hk\ (h+k)}{(h^2+k^2)^{3/2}}\ = 2\ \text{Cos}\ \theta\ \text{Sin}\ \theta\ (\cos\theta + \text{Sin}\ \theta)$$

if we write $h = \rho\ \text{Cos}\ \theta$, $k = \rho\ \text{Sin}\ \theta$

and $\therefore$ ε does not tend to zero as $\rho \longrightarrow o$ for all values of θ. So it is natural that the Formula IV should fail.

It is usual to take the continuity of both $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$ as sufficient conditions for the differentiability of $f\ (x, y)$. [See Bombay University Questions "If $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$ are continuous at (x, y) show that $f(x, y)$ is differentiable at (x, y)" 1937 B.A. Hons. also 1939 B.A. Hons.] It is possible however to prove quite simply that the continuity of only one of them (and the *existence* of the other) is sufficient for the differentiability of $f\ (x, y)$.

For the sake of definiteness suppose $f_x\ (x, y)$ is continuous at (x, y). Then $f_x\ (x, y)$ will exist in the small neighbourhood of the point (x, y). Now

$$f(x+\delta x, y+\delta y)-f(x, y) = [f(x+\delta x, y+\delta y)-f(x, y+\delta y)]$$
$$+ [f(x, y+\delta y)-f(x, y)]\ldots\ldots\ldots\ldots\ldots V$$

By the law of the mean we can write $f(x+\delta x, y+\delta y)-f(x, y + \delta y)$
$$=\delta x\, f_x\ (x+\theta\,\delta x, y+\delta y) \qquad o < \theta < 1$$
$$= \delta x\ [f_x\,(x, y)+\varepsilon]$$

where $\varepsilon \longrightarrow o$ as δx, $\delta y \longrightarrow o$ since $f_x\ (x, y)$ is continuous at (x, y)

Secondly, since $f_y\ (x, y)$ exists we can write

$$f(\,x,\,y+\delta y)-f\,(x,\,y)=f_y\,(x,y)\ \delta y+\varepsilon'\delta y \text{ where } \varepsilon'\text{->}o \text{ as } \delta y\text{->}o$$

So we can write V in the form

$$f(x+\delta x, y+\delta y)-f(x,y)=f_x(x,y)\delta x+ f_y(x,\ y)\ \delta y+\varepsilon\delta x+\varepsilon'\delta y$$

$$\text{where } \varepsilon,\ \varepsilon'\text{->}o \text{ as } \delta x,\ \delta y\text{->}o$$

$$=f_x\,(x,y)\ \delta x+f_y\,(x,y)\ \delta y+p\quad (\varepsilon\ \text{Cos}\ \theta+\varepsilon'\ \text{Sin}\ \theta)$$

$$\text{if } \delta x=\ p\ \text{Cos}\ \theta,\ \ \delta y=\ p\ \text{Sin}\ \theta$$

$$=f_x\,(x,y)\ \delta x+f_y\,(x,y)\ \delta y+p\ \varepsilon''$$

$$\text{where } \varepsilon''\text{->}o \text{ as } \delta x,\ \delta y\text{->}o$$

and this is the requirement for the differentiability of $f(x, y)$ at (x, y).

The above discussion shows how superfluous it is to assume the continuity of $\dfrac{\partial f}{\partial x}, \dfrac{\partial f}{\partial y}$ for the differentiability of $f(x, y)$ and hence also for the validity of results I, II.

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CONDUCTOMETRIC DETERMINATION OF THE CONVERSION OF CHROMATES INTO DI-CHROMATES

By

G. N. KADHE AND N. L. PHALNIKAR

A REVIEW of the literature shows that there are various methods of identifying and estimating chromates and dichromates in the presence of one another; the methods depend upon the use of (i) Absorption spectra (N. R. Tawde and G. R. Paranjpe, Indian J. Physics 1930, 4, 533-538) ; (ii) Potentiometric titration (L. E. Sabinina and A. K. Moralev, J. Appl. Chem. Russ 1939, 12, 301-308); (iii) Titration of chromate by sulphuric acid with congo red as indicator (Sacher Chem. zentra 1917, i, 693). The last method is simple and accurate. Sabinina has studied the conversion of chromate into dichromate by sulphuric acid by following the change in pH values of the solution but in this method there is no sharp change in pH at the conversion point to enable one to note the exact end point and thus to calculate the quantity of sulphuric acid accurately.

We thought, therefore, of studying the conversion of chromate into dichromate by sulphuric acid by following the changes in the conductivity. We have found, that at the conversion point of chromate into dichromate, there is a sharp change in conductivity. We have also carried out the above titrations starting with a mixture of sodium carbonate or sodium hydroxide and sodium chromate corresponding to the liquor obtained in the manufacturing process. In this case also the conductivity measurements have shown that the conversion point can be exactly determined.

We think, therefore, that this method being physical is to be preferred to that of Sacher (*loc. cit.*) and is more accurate than that of Sabinina (*loc. cit.*).

This method may be conveniently applied as a conductometric method for determining the amount of sulphuric acid required to convert sodium chromate into sodium dichromate in the manufacture of dichromates in which an excess of sulphuric acid would lead to the formation of sodium bisulphate.

In industrial practice the conductivity need not be actually measured as the graph of resistance of solution against sulphuric acid also indicates the end point. Also the conductivity apparatus is not so costly. We have found that the titration can be carried out accurately even on a student-type Wheat-stone bridge.

3 (a)

EXPERIMENTAL

Merck's pure chemicals were used in all the measurements. Conductivity water (Conductivity of water of the order $1 \times \overline{10}^6$ mhos.) was used for preparing the solutions. Measurements of electrical conductivity were carried out at 30°C in a cell (cell constant 0.1037) with an L and N Kolhrausch bridge and a carefully calibrated resistance box. Sodium chromate required was prepared by exactly neutralising chromic acid by sodium hydroxide. 10 cc of a standard solution of chromic acid were introduced in a flask and varying amounts of a standard solution of sodium hydroxide were introduced and the volume made up to 50 cc and the conductivity of the solution measured. Then the quantity of sodium hydroxide required for the formation of sodium chromate was estimated by a conductometric titration. This value agreed very well with the theoretical value.

Then 10 cc. of chromic acid and the exact quantity of sodium hydroxide required for the sodium chromate formation as determined above, were taken in a flask and to it varying amounts of sulphuric acid were added and the volume was made up to 50 cc and the conductivities were determined. Thus the titration of sodium chromate with sulphuric acid was followed conductometrically and from the graph of cc of $H_2 SO_4$ added against specific conductivity, the cc of $H_2 SO_4$ required for conversion of chromate into dichromate were determined and compared with the cc of $H_2 SO_4$ required theoretically.

The following table gives the titre, resistance of soln., and sp. conductivity in one typical experiment.

TABLE I

10 cc of $Na_2 CrO_4$ (0.022 Molar) was tritrated with
Sulphuric Acid (0.0279 Molar)

cc of $H_2 SO_4$ added	Resistance of Solution	Sp. Conductivity x 10-3
	ohms	
0.0	89.83	1.158
2.0	53.86	1.925
3.0	44.97	2.306
3.2	43.43	2.388
3.5	40.88	2.536
3.8	38.6	2.686
3.9	39.06	2.655
4.0	38.2	2.714
4.1	37.08	2.797
4.2	36.75	2.821
4.5	34.99	2.964
5.0	33.21	3.123

From the graph of titre against specific conductivity the quantity of $H_2 SO_4$ required for the conversion of chromate into dichromate is 3.9 cc (cc of $H_2 SO_4$ required by theory=3.943 cc of 0.0279 M).

Similar titrations of chromate solutions of different strengths with sulphuric acid were tried and the amount of sulphuric acid required for the conversion of the chromate into the dichromate was determined.

Titrations of chromate solutions containing a known amount of sodium carbonate were also carried out with sulphuric acid and the amount of sulphuric acid required for the conversion of a chromate into dichromate was determined.

The following table gives the strength of sodium chromate soln., the amount of sodium carbonate and also the amount of sulphuric acid required for the conversion.   The last column gives the amount of sulphuric acid theoretically required for the conversion.

TABLE II

	10 cc of Na_2CrO_4	0.013 M Na_2CO_3	0.01106 M H_2SO_4 (observed)	0.01106 M H_2SO_4 (calculated)
I	0.01630	..	7.4 cc	7.37 cc
II	0.0099	..	4.5 cc	4.476 cc
III	0.0099	3.0 cc	8.0 cc	8.002 cc
IV	0.00851	..	3.8 cc	3.839 cc
V	0.00851	3.0 cc	7.4 cc	7.365 cc
VI	0.022	..	9.8 cc	9.945 cc
VII	0.022	6.1 cc	17.00 cc	17.114 cc
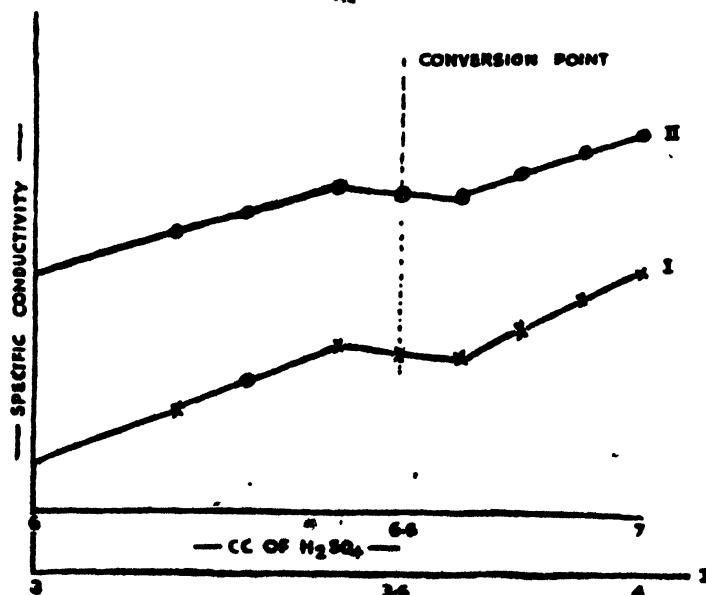
Fig. 1

Curves I and II (Fig. I) are titration curves representing the specific conductivity of sodium chromate alone and with sodium carbonate with the progressive addition of sulphuric acid. It will be observed that there is a sharp break when the chromate is changed to dichromate and also the conversion of chromate into dichromate can be followed conductometrically even in presence of sodium carbonate.

Similar titrations were carried out on sodium chromate liquor obtained from a Bombay factory. The liquor being concentrated, had to be diluted to a known volume, and the amount of sulphuric acid required for the conversion of chromate into dichromate was determined as above. We have found that this conductometric method is quite reliable.

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SOIL SOLUTION STUDIES IN IRRIGATION PRACTICES

(WITH SPECIAL REFERENCE TO ALKALINE AND SALINE SOILS)

By

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CONTENTS

I. INTRODUCTION

A LKALINE (solonetz) and saline (solonchak) soils appear in almost every part of our globe and are evidently attributed to certain climatic and irrigational conditions. It has been universally laid down that these soils occur chiefly in regions of limited precipitation and are characterised by accumulation of sodium and magnesium bases such as may endanger the growth of cultivated crops.

The question of reclamation and utilization of alkaline and saline soils has received a certain amount of attention in India both from agricultural and irrigational authorities and the subject has assumed greater prominence where modern perennial irrigation schemes have been put up.

Lower fertility or entire infertility results from chemical, physical and biological properties caused by the presence of injurious bases in these soils. Investigations into the nature of these soils record the fact that they are comparatively richer than salt free soils, in potash, phosphate, lime and other plant nutrients. Their unsuitability for a good crop growth arises not from want of food but their high sodium content either in soluble or exchangeable form. Reclamation and utilization of such territories is of great importance and presents the most important problem of the day.

A suitable and adequate supply of irrigation water provides one of the most important means of reclamation. But it is of utmost importance to know the nature and type of alkali soils in question before resorting to any reclamation means It is also equally important to know the "soil dynamics" summarising all the physico-chemical and biological changes that are continually occurring in soil due to weathering, irrigation, salt accumulation, drainage, evaporation and the soil population.

It is observed that there is no stability in soils, except in rare circumstances A continual evolution, indeed, goes on in the soil, and it is this dynamic character of soils that makes the elucidation of their reactions to reclamation measures somewhat difficult. Unless the new treatment of the soil dynamics is such as to lead to a normal agricultural soil, the reclamation will not be complete, although possibly temporarily effective, and the reclaimed soil will deteriorate again.

The practical value of a knowledge of the dynamics of alkali soils lies in changing the course of soil evolution and soil dynamics into the desired channel, and the natural forces in the reclaimed soil will assist in bringing the treatment to a fuller success. Thus there is a close connection between soil dynamics and the reclamation of alkali soils.

A technique is developed by the writer for the examination of salt movements and their effects on soils. With the help of small drain-pipe lysimeters, as described in the following pages, most of the vital points of problems likely to arise in connection with the irrigation scheme or reclamation are best calculated to yield essential information on submission to laboratory experiments. The work aims to contribute extensively to the solution of these problems.

II. PRINCIPAL OBJECT OF THE INVESTIGATION

The object of the research was initially to examine critically the findings contained in a previous paper by Mulwani and Pollard (1939) on soil solution studies and establish these methods in the investigations of alkaline and saline soils. The writer has stated that it is not valid to assume in all cases that an aqueous extract of soil in whatever soil-water ratio represents the liquid round about the soil particle. To this end it provided evidence and opened up further lines of study. Incidentally the findings contained in the paper corroborate experience of other workers. Viswanath (1939), and McGeorge (1937) have strengthened the writer's observations that the methods of base-exchange and pH determination now agreed upon as international ones, are not applied to soil conditions at a low soil moisture content.

Finally, however, it has been the principal aim of the writer to find out by means of small handy lysimeters made up of drain pipes, a simpler technique to determine the true status of the degree of salinization or alkalization under irrigation conditions and to observe the relative movement of bases and other fertility constituents resulting from downward percolation and upward movement of waters through various types of soils.

III. METHODS EMPLOYED

(a) Preliminary field survey :—

A preliminary soil survey of the land under investigation is made and the detailed observations planned out in the form of a map. The worst saline and alkaline patches located by means of such soil surveys have been excluded from irrigation where the commanded area has been greater than could be irrigated by the supply of water available.

Soil samples are then taken out from the mapped areas and labelled with a full description to depth of sampling and the history of the land under consideration. The soils are brought to the laboratory and subjected to the methods of analysis as suggested by Mulwani and Pollard (1939).

(b) Lysimetric study :—

The lysimetric technique of studying soils under irrigation conditions has been followed after determining the original state of the soils through a consideration of the displaced soil solution. The drain pipes (vide plates I—III) representing lysimeters are filled with soil from the surveyed area in natural layers with careful packing at about 10 per cent. moisture content. For reclamation purposes soils containing salts under natural or artificial conditions are packed into the lysimeters and subjected to normal irrigation doses with fresh (distilled) and saline waters. Controls containing salt free healthy soils are also prepared and examined in a similar way.

The investigation has been divided into two parts. The first part is devoted to the study of the relative movement of bases and other fertility constituents resulting from downward percolation of saline and fresh

water through healthy and saline soils. The usual irrigation doses as given to dry crops are given at the surface. The second part of the investigation is designed in a similar manner but the object in this case has been to examine the influence of the upward movement of saline and fresh waters through initially healthy and saline soils. The water is, therefore, applied to the bottom of the soil column. Further details of these are given under "experimental" heading.

(c) Pot culture and field trials :—

In response to the general criticism by agronomists that little or no use has been made of soil analyses, the soil solution studies have further been extended to determine the relationship of crop yield to the nature and amount of the nutrient elements in the soil solution.

In this connexion soils yielding poor, medium and luxuriant growth of crops are taken from the field. An attempt has been made to collect data to examine the practical utility of soil solution technique as applied to pot culture and field tests on soils of different fertility gradient.

IV. SOILS USED IN THE INVESTIGATIONS

English (Devonshire) and Indian (Sind, Punjab, and Delhi) soils were taken up for the study and examined by the methods described. A short description of the soils may be given : English (Devon) soil was obtained from pasture land of Greenwell Farm and the detailed description is given by the writer (vide Ind. J Agric. Sci., 9, 1939, 486). The soil is derived from Tertiary rock and is of old red sand stone.

Indian soils—

(i) *Sind* —Soils of different types were obtained from the Agricultural Research Station, Sakrand, Sind. Their composition and description is given in the above-mentioned publication.

(ii) *Punjab*—Soils were obtained from (a) Bara Farm, Montgomery, (b) Muzaffarabad Alkali Lands, Multan, (c) Sahiwal Alkali Lands, Shahpur. All these soils were intensely alkaline with 0.8% to 2.5% total salinity and 0 3% to 1 0% sodium carbonate. The detailed descriptions of these soils are given by Lander (1929).

(iii) *Delhi*—The soils were sandy, non-saline, with a low water holding capacity. The soils were also poor in potash. The object of including these soils was to study their behaviour on treatment with different salts of calcium and sodium and also to study the effects of water at different soil-water ratios.

V. EXPERIMENTAL

A preliminary survey of the soil solution methods was made by the writer in the previous paper. Further tests have been carried out to study the possibility of applying these methods along with newly evolved lysimetric technique to the investigation of factors contributing towards soil productivity, exhaustion and deterioration.

' The experiments carried out are divided into the following sections, *viz.*—

(a) Comparison of aqueous extracts and displaced soil solutions.

(b) Examination of soil moisture under field conditions.

(c) Selection of a suitable size of lysimeter to imitate field conditions to measure soil alkalinity and general fertility.

(d) Salt and irrigation :—

Soil solution methods and lysimetric technique are applied in irrigation practices and in the investigation of soil reactions.

Movements of water in different types of soils.

(e) Pot culture trials.

(f) Field tests.

Each part of the investigation has been summarised in the following order with its data compiled in the appendix.

(a) Comparison of aqueous extracts and displaced soil solution in different types of soils :—The following soils were taken up for the study—

(i) Natural healthy soils from Delhi and Sind,

(ii) Natural alkaline soils from Punjab and Sind, and

(iii) Artificially salted soils from Delhi.

The results of the soil solution analyses obtained with the above mentioned soils are recorded in Tables; I, II, III. IV, and IV (*a—c*). It is observed that considerable divergencies occur between the amount of soluble matter in soils determined by means of soil extracts and those determined with soil solutions. The results confirm the findings contained in the previous publication on the subject. With the widening of the soil water ratio there is a general increase in the apparent values of the soluble calcium, potassium, phosphate, and total soluble matter, a, less marked increase in magnesium and little change in sodium. The values for base ratios, calcium-sodium and calcium-magnesium increase and those for sodium-potassium decrease rapidly as the portion of water is increased. It is also interesting to note that the high alkalinity due to sodium carbonate shown in soil solution of alkali soils disappears in the extracts in most cases.

In general there seems no continuity between the variations in values obtained with the different soils in water extracts and that appearing in the corresponding displaced solutions.

Special mention may be made of the interactions of various salts on Delhi soils. The details of various salt and water treatments along with the results of analyses are shown under tables (IVa—IVc). Table IV records the analyses of untreated original soil and table IVd records the calculated amounts of ions added to the soil under different salt treatments as shown under Tables (IVa to IVc).

Summing up, the soil was treated with common salts occurring in alkali and saline soils. To have a clearer idea about the reactions, the soil in separate lots of 20 lbs. was treated with different salts of sodium and of calcium at different concentrations. Two more lots of soil were treated with mixture of salts to imitate saline and alkaline soils commonly occurring in arid regions. The salt treatments were further multiplied by addition of water at soil solution (about 15% water content), and at 1 : 1 and 1 : 5 soil-water ratios.

Following reactions have been recorded :—

(1) Displacement of calcium by sodium salts :—

Both sodium chloride and sodium sulphate displace calcium from the soil complex. Sodium chloride is comparatively stronger in this action. Sodium carbonate has reverse reaction on soil calcium. On the other hand it precipitates as much equivalent amounts of soluble calcium. Soil solution obtained under 1% salt treatment gave following results :—

Treatment	Calcium (p.p.m.)
Na cl 1%	552
Na_2SO_4 1%	65
Na_2CO_3 1%	10
Control	42

(2) Effect of water on calcium in salted soils :—

Larger doses of water in general displace larger amount of calcium in the salted soils with the exception of sodium chloride and calcium chloride treatment. In these cases perhaps reverse reactions take place. Calcium of the resultant calcium chloride is partly absorbed by the soil. This point needs further investigation.

(3) Effect of water and salt on soil phosphates :—

(i) In case of salt free healthy soil larger dose of water has greater solvent effect. Phosphate content as represented by 1 : 1 soil water ratio was four times higher than the amount shown by soil solution displaced at 15% moisture content. Soil solution gives 0.5 p.p.m. phosphates whereas water extract calculated to 2 p.p.m.

(ii) Under lower soil moisture content as met with under field condition sodium chloride depresses the solubility of phosphate whereas sodium sulphate and sodium carbonate increase the same. Phosphates as obtained by sodium chloride, sodium sulphate and sodium carbonate treatments are 0.2, 3.0 and 5.0 p.p.m. respectively. The untreated soil give 0.5 p.p.m. PO_4 calcium chloride like sodium chloride depresses the solubility of soil phosphates. Calcium sulphate and calcium carbonate release it or turn it more soluble. Order of solubility of the three calcium salts is 0.3, 4 and 6 p.p.m. respectively.

(4) Effect on Magnesium :—

Larger doses of water dissolve larger amounts of magnesium from soil. Sodium chloride and sodium sulphate displace magnesium. Sodium carbonate depresses the solubility and displacement of magnesium.

(5) Interactions with sodium :—

Three concentrations of sodium in different salt forms were used. Table IV (d) shows the worked out amounts as 390, 1950, and 3900 p.p.m. of sodium for 0.1%, 0.5% and 1.0% salt treatments respectively.

Adsorption and absorption of sodium from sodium sulphate and sodium carbonate is greater than it is from sodium chloride. Perhaps the calcium sulphate and calcium carbonate formed reduce the solubility of sodium of original soil and consequently help the adsorption.

Similar reactions are recorded from calcium salts treatment. Calcium chloride comparatively displaces larger amounts of sodium from soil than calcium sulphate and calcium carbonate. At 1 : 1 ratio the displacement of sodium by calcium is maximum. However, increased concentrations of calcium salts do not accelerate this reaction.

(6) Interaction between mixed salts and the soil :—

Amounts of calcium added in form of calcium carbonate and calcium sulphate are shown in Table IV (d). Amounts of calcium recovered with different soil water ratios are shown under table IV (c). In all 11500 p.p.m. of calcium (1500 in soluble form and 10000 in insoluble form) have been added whereas amounts recovered are 133, 487 and 941 p.p.m. with different soil water ratios. Evidently the soil adsorbs all the calcium carbonate and also most of calcium in form of calcium sulphate. Larger amounts of calcium come in solution with widening the soil water ratio.

Adsorption of magnesium is still greater. It may be due to partial precipitation of calcium and magnesium salts on addition of alkali salts of sodium. However, it has been observed that sodium salts in mixture displace soil calcium in which case precipitation is not possible. It is noteworthy that the sodium carbonate up to 0.1% concentration in combination with other salt does not retard displacement. Individually as shown in Table IV (a), it not only affects the displacement but precipitates appreciable amounts of calcium in soluble form.

Unfortunately the Delhi soil used in investigation was very light and sandier type of soil. The reactions will be of striking nature if heavier clayey types of soil are examined under salt and irrigation conditions.

(b) Examination of Soil Water under Field Conditions

In an arid region like Sind in a dry year the natural moisture content in a virgin plot was found to be of the order as shown in Table V. Moisture contents were examined up to a depth of 12 feet during hot and cold seasons before and after an irrigation dose of six acre inches.

It was observed that in a virgin plot, the moisture in the upper two feet is 2% before irrigation. The moisture content rose to a maximum value of 19% after an irrigation dose of six acre inches. Almost all irrigation experiments, results of which could not be given for want of

space, have shown that the moisture content rarely rises above 20% under normal conditions. This represents 5 : 1 soil-water ratio as against customary 1 : 5 ratio used in the examination of alkaline and non-alkaline soils. Soil solution as described is soil water displaced from a soil having 20% or less moisture content. It has been shown that the safety limits used in practice of water extracts are purely empirical and their application to different soils is of doubtful value in this point. Soil solution gives the most reliable information in all types of soil. It evidently yields more or less true representation of the liquid phase in soils and therefore forms the nutrient medium of crop.

(c) LYSIMETRIC TECHNIQUE—SIZE OF THE LYSIMETER

Masonary Tank lysimeters for measuring losses of nutrients in drainage are designed at various Agriculture Institutes and Universities. Three drainage gauge-lysimeters were constructed by Laws and Gilbert at Rothamsted in 1870. They have been used, in addition, to determine the losses, to measure the proportion of water which percolates through different depth of soils. Lysimeter drain-gauges were constructed at Craib-stone, Scotland College of Agriculture, in 1914 to observe the nutrient requirement of soils and crops and also to know various soil reactions. The information obtained by means of such drainage gauges is of immense importance.

It is, however, impossible for every soil scientist to have within easy reach such tank lysimeters. Moreover such permanently fixed up lysimeters are of little value when a large number of soils are to be examined in a short time under different irrigational or manurial treatment. It became necessary therefore to adopt suitable and handy small scale lysimeters.

Miniature lysimeters of three different sizes were tested by the writer under controlled conditions. The smallest size was a twenty ounce bottle with an open bottom as per illustration (*vide* plate I). The medium size was made up of a drain pipe of six inches diameter and one foot height. The larger size measured seven inches internal diameter and three feet unit height. In some cases three small one foot pipes were connected to give one lysimeter. All the three sizes were examined with similar soils. Drainage solutions and leached soils after irrigational treatments were tested and the results critically examined and compared with those obtained under normal field conditions with similar treatments. Usual irrigations were given. The amounts of water were calculated on the basis of acre-inches given to cold weather crops in arid regions, the actual distribution, according to requirements was six inches, four inches, and four inches to make total amount of fourteen acre inches of water. One litre leachings in the three lots were collected from each series of lysimeters and various determinations made. The results obtained with non-alkaline and alkaline soils in three types of lysimeters are shown in Tables VI and VIa. The results of displaced soil solutions and corresponding water extracts are also included in these Tables for comparison.

In the case of alkaline and saline soil (Table VI) abnormal results are recorded with smallest size. Large amounts of calcium, potassium

and phosphates are removed from the soils of bottle lysimeter and the first leachate removes most of the soluble matter. In the case of large three feet size lysimeter the removal of the soluble matter is more or less regular and the drainage solution resembles the displaced soil solution. Summing up the observations, the leachates obtained with the smallest vessel resemble 1 : 5 soil-water extracts of the same soil, and medium size lysimeter leachates compare with 1 : 1 extracts. Under natural conditions it would hardly be said of soil being exhausted with normal irrigation as noted in the smallest miniature bottle drain-gauges. Similar discrepancies in the case of normal soil (Table VIa) are recorded and data obtained, lead to the conclusion that three feet drain-pipes fixed in suitable racks are satisfactory for the examination of all types of soils.

In order to secure further evidence with regard to the suitability of the large size drain-pipe lysimeters the downward movement of moisture and soluble matter was examined in the lysimeter soil and in the same soil under field conditions. In this part of the experiment five one foot pipes were connected to give a unit five feet drain pipe and this was filled with soil. A dose of six inches of water was applied on the top of this pipe and also to the plot having similar soil layers. Under natural conditions the six inches irrigation penetrated three feet in twenty-four hours and five feet in forty-eight hours. In the drain-pipe lysimeter the time taken was slightly less. It took twenty hours for three feet moisture penetration and forty-two hours for five feet.

Moisture contents and bacterial activity at the end of the experiment were, however, found to be practically of the same order as shown below :—

| Layer | Plot | | Drain-pipe | |
	Moisture%	Bacterial No. per grm. soil	Moisture%	Bacterial No per grm. soil
0-1'	14	620	15	580
1'-2'	19	1100	17	1080
2'-3'	19	3200	17	3100
3'-4'	18	6400	18	6200
4'-5'	16	18000	19	16000

The soils from the plot and the pipe were examined through considerations of displaced soil solutions. The results obtained are shown in Table VI b. The observations show that the changes occurring in the drain-pipe soil are similar to those that take place, due to irrigation, in the same soil under natural field conditions. Very minute differences in the figures may be due to experimental error.

This preliminary investigation indicates the satisfactory nature of soil solution methods, and small scale lysimeter technique in the exam-

ination of soils with regard to their fertility (and alkalinity in the case of alkaline soils) as found under normal field conditions.

(d) SALT AND IRRIGATION

(i)   *Soil solution methods and lysimetric technique :—*

This section of the work deals more particularly with changes taking place under irrigated conditions both of healthy and salt-treated soils, and has been directed towards obtaining information as to relative movement of bases and other important soil constituents resulting from upward and downward movement of saline and fresh waters. Trials were made initially with fresh and with artificially salted soils from Devon (England), and in the second part of the investigation with three types of natural soils from Sind (India).

In some of the experiments conditions similar to those occurring under irrigation schemes have been imitated as far as possible, and in others the influence of upward movement of the saline drained waters through initially healthy soils have been examined. A series of eight drain-pipes lysimeters were filled for the experiments. A batch of these is shown photographically (*vide* plate III).

The treatment of the eight large three feet pipes was as under :—

(1)   Control (moist soil only, with 20-24% water) ;

(2)   Control (salted moist soil with 1% Nacl).

These were not irrigated but kept as controls to record any changes which might result from the packing of the soil in this manner during the experimental period. The remaining six sets were allotted to two parts of the investigation. The first series (3—5 pipes) was devoted to the study of relative movement of bases and other important constituents resulting from the percolation of saline and fresh waters through fresh salted soils from Devon. The usual irrigation was given at the surface. The amounts of water were calculated on the basis of the acre inches of irrigation water given to a cold weather crop in arid regions. The actual distribution of water according to requirements, was as mentioned in the previous section 6 inches, 4 inches, and 4 inches to give a total amount of 14 inches of water. The leachings in three lots were collected from each series and bases and other ions washed out were determined in each case (Table VII). The full columns of soil left after leachings were broken into layers and the soil solution from each layer was examined. The compound pipes assigned to this part of the experiment were utilised thus :—

(3)   Normal soil treated with distilled water ;

(4)   Salted (1% Nacl) soil treated with distilled water ;

(5)   Normal soil treated with (salt 1.5% Nacl solution) water.

Each pipe held about 20 lbs. of soil.

The other part of the investigation (6—8 pipes) was designed in a similar manner, but the object in this case was to examine the influence of the upward movement of saline and plain waters through initially

healthy and salted soils.   The water was therefore applied at the bottom of the soil column in the following arrangement :—

    (6)   Capillary rise with distilled water through original soil ;

    (7)   Distilled water through salted (1% Nacl) soil ; and

    (8)   Salt water (1.5% Nacl solution) through original soil.

The soil columns after four weeks period were separated and the displaced soil solution examined.

The columns of soil in the pipes (3 to 5) left after leaching, were broken into three layers and examined for the distribution of the bases and other constituents of the displaced soil solution obtained from these leached layers of soil.

However, pipes 3 and 4 failed to yield sufficient soil solution from some layers, perhaps due to deterioration of the leached soil (Gedroiz 1924). Two to five p.p.m. of Fe were obtained from these layers, particularly where soluble sodium is leached.   Sufficient soil solution was obtained from the surface layers of these pipes and the figures of analyses are given in Table VIII.

Pipe No. 5 was saturated with sodium and the soil from all layers yielded sufficient quantities of solution owing to the coagulating effect of soluble electolytes as also explained by Kelley (1925).

Pipe No 3 *vide* Table VII.

WATER LEACHING OF FRESH SOIL UNDER IRRIGATION CONDITIONS

The fact that the third leaching is not very much lower than the first is in conformity with the less severe treatment given.   Organic nitrogen tends to increase in later leachings probably due to the breakdown of the organic complex of the soil.   Potassium, chlorine, and sodium tend to decline in the later leachings, but the decline in K and CI is relatively greater than that of Na.

Pipe No. 4 (1.0% Nacl treated soil), was irrigated with fresh water. A slightly greater removal of total and organic nitrogen is observed. The change in bases (except sodium) of the successive layers is not remarkable.   The decline in chlorine concentration is much greater than that of sodium.   Phosphate reappears in soluble form in surface layers as sodium chloride is washed down.

In pipe No. 5 the use of saline water also increases the removal of organic nitrogen and bases, potash being less affected than calcium and magnesium as judged by differences from the values of pipe 3 and also the relative differences in the three successive leachings in pipe 5.   Apparently the action on potash and phosphates is either smaller or less rapid.

In pipe 4 the base exchange reactions, between salt and soil, are completed prior to leaching, and in this case the changes in concentration of K of the leachings are similar to those of the other bases.

Slower exchange rather than slower movement in the soil column is probably the cause of the relatively slower leaching of K in pipe 5.

RESIDUAL SOIL SOLUTION FROM LEACHED SOILS

The surface sections of the leached soils in which the effect of irrigation may be expected to be most definitely marked yield soil solutions (Table VIII) which in general reflect the conclusions drawn from the analysis of the leachates. The depletion of bases falls less heavily on K than on Ca and Mg (compare 3 and 4 leached soils). In pipe 5 the action of salt solution is much less complete than in pipe 4, the lower sections still showing the effects of base displacement rather than of leaching. Here also the slower removal of K than of Ca and Mg is apparent.

The breakdown or dispersion of organic nitrogen is also shown, the values, even after leaching, being higher in the salt treated than in the control soil.

The determination of Fe and Al in these solutions shows that Nacl treatment tends to bring these bases into solution. Leaching alone brings Fe into the soil solution and this effect is intensified by the presence of Nacl.

The transformation of insoluble Al into soluble Al by the action of Nacl occurs much more readily than that of Fe. Moreover, the soluble aluminium once formed is much more easily leached than is Fe. In pipe 5 it would seem probable that the soluble Al produced is already being leached (high values in bottom layer), whereas the liberation of Fe is only just beginning in the surface layer.

In pipe 6 (*vide* Table IX) the upward movement of water through normal soil carries with it Ca, Na, Al, Po_4, but not K or organic matter or Fe. In the case of Fe and organic nitrogen it would seem probable that these constituents only appear in the soil solution as the result of prolonged passage of water through the bottom layer and follow the removal of the majority of the bases.

In pipe 7 (*vide* Table IX) in spite of less water having passed up the column (Fig. I) the upward movement of bases towards the top layer is more definitely marked. In this case, unlike that of pipe 6, organic nitrogen and K have also moved on the surface, K in relatively smaller proportions than those of Ca, Mg and Na. No definite evidence of movement of Al is apparent. As before, the removal of Nacl by water has increased the solubility of Po_4, the bottom layer naturally showing the highest values.

Traces of Fe have also appeared in the bottom layer as in the case of pipe 6.

THE PASSAGE OF SALT WATER THROUGH NORMAL SOIL

Pipe 8 shows the same general effects as in pipe 7, the action in this case being most marked in the lower layers effective concentration of salts not having reached the upper section.

The more outstanding effects of Nacl observed in the experiments on the Devon soil are (1) reversible depletion of soluble Po_4 : (2) relatively slower displacement and subsequent leaching or capillary rise of K than of other bases : (3) movement of organic nitrogen constituents and Fe : (4) and movement of Al only in soils of low Ca Co_3 content.

SIND SOILS

Having known the general effect of Nacl on English soil under conditions similar to those occurring under irrigation and water logging, the investigation was further extended to the study of three types of natural soils from arid regions of Sind (India). All soils are from Indus Valley.

Soil A.—Has been taken from a normal high yielding plot under wheat and cotton.

Soil B.—Is slightly saline, giving a poor yield of cotton.

Soil C.—Is taken from a barren plot not permitting even the germination of seeds.

The chemical and physical composition of each type of the above mentioned soils is given in Table X. All the soils in general are poor in phosphoric acid and nitrogen. Soil C, however, contains large amounts of nitrate nitrogen with other salts. Soil A is a light type of soil and has the highest Ca : Na ratio, and is free from excess of injurious substances. Soil C on the other hand, is a heavier type of soil, has the lowest Ca : Na ratio, and a higher PH value. Soil B is an intermediate type.

The soil samples of five sub-soil layers, each one foot in height under each of the mentioned plots, were examined. The salt content of each layer and its sand content is recorded in Table XI.

Characteristic differences in the three types are again apparent. "A" has fairly free drainage and irrigation has carried the soluble salts down to a depth below 6′. "B" is a heavier type in which drainage is inferior and high surface concentrations of salts are apparent. "C" has still higher concentrations of salts near the surface, and shows evidence of further accumulations at lower depths.

LYSIMETER EXPERIMENTS

The soils were packed in lysimeters about two weeks after moistening with water and leached with three successive amounts of water corresponding to the normal irrigation treatment.

Analyses of leachings and of the soil solutions obtained from the leached soil are shown in Tables XII, XIII, XIV.

The large volume of leachate from the saline soils C is partly explained by its initially higher water content, 15 per cent. as against 14 per cent. in B, and 10 per cent. in A, and partly by the fact that during leaching the soil gradually settled into a more compact mass, shown by sinking in the pipe (not shown by A or B). Not very great difference was found in the water retaining capacity of three soils, *viz.*, A, 30.5; B, 32.2; C, 33.5%. It may also be that some channelling occurred during the settling of the soil C in the pipe.

In a separate examination of percolation rate interesting results (*vide* Table XV, fig. 2) were obtained. The rate of percolation and the volume of leachate were initially much higher in C than A. With more prolonged leaching the percolation became gradually slower in C, and finally reached values much less than in the case of A.

Presumably the higher total salt content of the soil water in C tends to maintain flocculation of Na clay and its anticipated effect in regarding percolation is marked. With the removal of the soluble salts by leaching, the soil becomes more and more deflocculated and impermeable. The larger amounts of leached salts in the case of C are to be expected from the large quantity originally present and from the fact that a much larger proportion of the irrigation water passed through this soil, than through A and B. In most cases the small differences between the relative and actual concentrations of basis, etc., in successive leachings coupled with the facts that no Fe, Al, or Mn appeared in any of the extracts, and that the PH change is small, indicates that the ordinary sixteen acre-inch irrigation is unlikely to bring about changes sufficiently severe to involve movement of Fe, Al, and organic matter as in the Devon soil, or any appreciable change in soluble phosphate content. In the saline soil C, and to a smaller extent in B, the rate of removal of total soluble solids in successive leachings is largely accounted by Nacl It is to be noted, however, that in A and B the initial rate of removal of Cl is much greater than that of Na whether considered on the basis of concentration in leachings or as absolute amounts In A and B, third leachings, the Na and Cl concentrations have approached to those equivalent to Nacl. In C, however, the first leaching contains Na and Cl in approximately equivalent proportions, whereas in the second and third leachings the Na concentrations become increasingly greater than the equivalent Cl concentrations. In no case does the originally low Po_4 value increase as leaching proceeds At this rate of irrigation removal of Nacl does not reach the stage at which an increase in Po_4 solubility can occur.

BASE RATIOS IN LEACHINGS

The principal differences in the base ratios of the leachings are the higher Ca : Na and Ca : Mg in the normal soil, and the high Na : K in C.

In general, the ratios Ca : Na, Ca : Mg do not alter to any great extent in successive leachings Na : K values remain steady in A and B, but change somewhat irregularly in the saline soils

The leaching of the soils, therefore, has led to the removal of bases in characteristic proportions which are of the same order as those in the soil solution from the original soil Leachings from the saline soil are relatively poor in Ca and high in Na, and the Ca : Mg ratio is notably lower than in the normal and intermediate soils. The Na : K ratios follow the range of the salt contents of the soil.

The soil solution remaining in the leached soils give a somewhat different view of the effects of irrigations. A comparison of the two extreme soils A and C shows that although the original soil solution from the saline soil had much higher concentrations of solutes than those of A, the larger proportion of irrigation water passing through the soil had brought about a greater percentage lowering in the concentration of total solids, K, Na and alkali carbonates than occurred in A. On the other hand, the percentage increased in concentrations of Ca, Mg, carbonates and NO_3 is greater in the normal soil. The percentage changes in Mg and Cl concentrations are similar in both soils.

Since the concentration of bases in the soil solution represents an equilibrium with the exchangeable bases of the clay complex, the effect of leaching on C must be taken as showing a rearrangement of the proportion of adsorbed bases with an increase in the proportion of Ca and Mg at the expense of Na and K, and a very marked improvement in the Ca Na ratio. On the contrary in A the changes, although smaller in range seem definitely to be of an opposite character. Changes in the Na : Ca ratios of the two soil solutions serve as a measurement of these effects. Irrigation, therefore, tends to improve the base ratios in the saline soil C and to affect that of A adversely, except on the surface 1 foot, in which the leaching is most severe. Here the accuracy of the low value for Na renders the significance of the calculated Ca : Na ratio somewhat doubtful. Values in soil B are, in general, immediately between those of A and C.

These conclusions confirm the practical results obtained in Sind that the irrigation exhausts the non-saline soils whereas it improves saline soils.

DUPLICATE LEACHING SET

All leachings are passed up in this part of the experiment. (For composition of leachings see Tables XII, XIII, XIV and XVI)

The results of the capillary return of the drainage water through the soils from which they were taken are shown in Table XVII Upward movement of salts is more extensive in saline soil C than in soils A and B. In the latter only the bottom layer showed serious change, whereas in C the middle layer was definitely affected, and in the case of Cl movement into the surface layer was apparent. Since all the original drainage water had passed back into the soil, and the water contents of the layers at the end of the experiment were below the retaining capacity of the soils, there must have been appreciable evaporation from the soil surface, *i.e.*, the returning water had penetrated the whole column, the movement of solutes, therefore, is considerably slower than that of the water in which they were dissolved. This may be due to base exchange reactions.

In the normal soil A, the leaching and subsequent return of the drainage water has resulted in a marked increase in Ca, Mg and K contents of the lower layer, whereas that of Na is definitely lowered at all depths.

Chlorides appear to move upwards more slowly than the bases. There is a decrease in all carbonates, more especially Na_2Co_3. These changes are reflected by the base ratios, Ca : Na and Ca : Mg decreasing towards the surface and Na : K showing no definite change.

In B similar changes are observed. Ca, Mg and K in upper layers are definitely higher than in the original soils, and the Na concentration is lower Mg : Ca carbonates show a decrease in all layers, whereas Na_2CO_3 shows an increase in the bottom section. •

In this case also the Ca : Na and Ca : Mg ratios increase towards the surface whereas Na : K shows the reverse variation.

In C, changes in individual base concentration in comparison with the original soil solutions are somewhat different from those in A and B.

The Ca concentration is definitely decreased. Values for Mg show a general increase especially in the lower layer. K, Cl, and Na concentrations in the lower layers are increased to more than double those of the original soils.

Carbonates show a considerable decrease in all layers, whereas the alkali carbonates increase to some extent in the middle and the lower layers.

The Ca : Mg ratios again increase towards the surface, whereas the Na : K changes in the reverse direction.

The net result of the combined leaching and capillary movement has been to improve the ratios of the surface layer, but to make the bottom layers still worse than the original   This is reflected in the frequently observed fact that in leached alkaline soils germination of seeds is often good but as soon as the roots of the young seedlings penetrate into the lower layers they succumb to the still marked salinity.

In general, the effect of the combined downward and upward movement of water has been to improve Ca : Na ratio of the lower layers of the normal soil, and of the upper layers of the saline soil.   At the same time there is some deterioration of the surface of the good soils and further deterioration of the lower layers of the saline type C.   The alkali carbonates have decreased at all depths.   Alkaline earth carbonates also decrease in A and B, but tend slightly to rise above the original values in C   The removal of Nacl by leaching is very considerable, the subsequent capillary movement tends to bring back Cl much more rapidly than Na, except in the case of saline soil in which Na and Cl reappear in the lower layers in approximately equivalent proportions

The final Na and Cl concentrations of the lower layers of the saline soil are approximately double the initial values, thus indicating that the sixteen inches irrigation is not only insufficient to cause any permanent improvement but may intensify the unfavourable condition especially in the sub-soil layers.

In B the final Na concentration is less than that of the original, whereas the final Cl concentration is approximately doubled till the bottom section

The fact that the upward movement of the leachates has increased the concentrations, of certain bases beyond the values in the original soil solutions is to be explained by average concentrations of the leachates (vide Table XVI) being greater than those of the original soil solution. The redistribution of exchangeable bases consequent upon the water movement in such that reabsorption cannot take place to the same extent as before.

FURTHER TRIALS

In order to examine the effects of a more prolonged capillary rise of water through soils in the distribution of constituents of the soil solution, pipes were filled with soil as before.   In one series distilled water and in another an artificially prepared saline solution comparable with an

alkaline leachate were used. The pipes were subsequently broken into sections and soil solutions examined. Results obtained with distilled water are shown in Table XVIII after a fifteen days' period.

It is seen that the soil solution in the surface layer of soil A has almost the same composition, as the original, whereas the lower layers show definitely lower concentrations. There is also a tendency shown more particularly in the total salt figures for the bottom layer to have somewhat more solutes than the middle layer. Presumably this is the immediate effect of the increased water content and is balanced against a rearrangement of the exchangeable bases in the upper two layers.

Under these circumstances, which correspond with a capillary rise approximately to more than double the normal irrigation dose, nonsaline soil undergoes little change other than a decrease in concentration of solutes below the surface.

In the intermediate soil B, capillary rise is more rapid and has induced a concentration gradient of nearly all solutes which rise towards the surface. The concentration of the soil solution of the surface layer is from 50—100 per cent. greater than that of the original soil This appears to affect all constituents of the soil solution except carbonates to roughly the same extent and differences in bases ratios are not marked, $i\,e$, there is no serious change in salinity.

In the case of carbonates, the relatively higher values for Ca, Mg carbonates in lower layers are characteristic and appear still more definitely in the saline soil C The Na_2CO_3 values show an upward gradient towards the surface but it is to be noted that all values are less than the original.

The effect of prolonged capillary rise of distilled water through a partly saline soil, therefore, seems to be to increase the total concentration of the soil solution from the surface layer without appreciable change of proportion of the solutes, and to decrease (also roughly proportionally) the concentration of the lower layers, with a tendency to build up a higher concentration of Ca, Mg carbonates (but not Na_2CO_3)in the lower layers In C, the tendency towards an increased concentration of solutes in the surface section is again marked The second layer is also affected to a much more marked degree than in B, which seems hardly to be accounted for by the somewhat greater amount of water passing upward. There are, however, marked differences in the base distribution of the upper layer in this case The concentration of Na, K, and Cl are definitely higher than in the original soil, but those of Ca and Mg are lower in all sections.

There is also a tendency for the bases, more especially Ca and Mg, to reach maximum concentration in the middle layer although the total salt concentration shows a much higher gradient in the surface than in the second layer. The marked lowering of concentration of nearly all constituents in the lower layer is again seen here. The Ca, Mg bicarbonates show a more definite increase in concentration with depth than was apparent in the intermediate soil type B.

In the case of Na_2CO_3, values in the surface layer are remarkably low but increase rapidly with depth. The bottom layer contains a much

higher concentration than the original soil solution, due presumably to increased hydrolysis of the Na'clay. The unexpectedly low values in the surface layer may possibly be due to precipitation of Ca and Mg carbonates (since Ca and Mg concentrations have decreased).

The capillary rise of fresh water through the saline soil has, therefore, resulted in a salt gradient in the soil solution, which rises towards the surface (except in the case of carbonates) an increase in actual concentrations of Na, K and Cl and a decrease in Ca and Mg.

This represents a deterioration in so far as total salt and Ca/Na ratio is concerned. The removal of Na_2CO_3 is marked only in the surface layer, the second being approximately the same as the original and the lowest showing a much increased Na_2CO_3 concentration.

In the second experiment a solution containing Ca, Mg and Na in proportions similar to those of drainage water from an irrigated saline soil was allowed to rise upwards through the soils A and B with a view to observing possible adverse effects (*vide* Table XIX).

In both soils, although the surface layers show marked increases in the soil solution concentrations, the maximum effect of the saline water is apparent in the middle section. On the basis of relative changes in total salt concentration it appears that the upward penetration of the saline water is more complete in the more saline soils, although the actual amount of water passing is somewhat smaller. This tendency has been observed throughout these experiments. On the other hand the relative increase in base concentration in the upper and middle layers is greater in the soil 'A'. Changes in the Cl concentration occur somewhat in advance of those in bases as the upward movement proceeds. The base ratios Ca, Na and Ca/Mg decline with depth and although that of the surface layer remain practically unchanged, sub-soil deterioration is indicated.

As in the previous experiment the proportion of Ca and Mg carbonates is decreased by the upward movement of the salt solution, and at all the depths is less than the original. Lowerings of Na_2CO_3 concentration is more marked in the normal soil.

The upward movement of saline water through the intermediate and normal soils affects a general increase in soluble matter at all levels up to the surface, and an adverse change in the Ca/Na ratio from the lower levels upward. Soluble phosphates disappear, the Ca and Mg bicarbonates decrease to a considerable extent. Na_2CO_3 in the soil solution is also decreased much more definitely in the case of the normal soil.

(ii) *Capillary Movement of Waters*

In the course of this work indication of differences in the rate of capillary movement of fresh and saline water through normal and saline soils were observed.

In order to clarify this question direct observations were made (1) in long glass tubes ; (2) in the drainpipe lysimeters. The results are shown in Tables XX and XXI (figs. 3 and 4). These show that saline water

rises more quickly than fresh water through the saline soil column, the difference being small in the case of the healthy soil. In the lysimeters the rise of fresh water occurred in a similar order, i.e., the rate decreases with the degree of salinity.

The initial period during which the rise through healthy soil somewhat exceeded that of the saline ones is probably occupied by the setting of the wet soil in the pipes and cannot be regarded as typical.

(e) POT CULTURE TRIALS

Two soils, one from high yielding fertile plot and the other from low yielding poor plot, were taken up for soil solution and wheat pot culture studies. The fertile soil was further leached in drain pipe lysimeter and included in the study. This soil received additional treatments with artificial fertilizers and with its own drainage solution (leachate). The details of the experiment with regard to the soil analyses and plant performances are consolidated in Table XXII.

There is definite relationship between the concentrations of the soil solution and the wheat yields. The experiment indicates that healthy soils decline in fertility on leaching. Fertilizers like sulphate of ammonia and super phosphate do not restore the lost productivity. However, treatment with its own leachate used as irrigation medium improves the soil practically to its original state as shown by analyses and yields. This confirms the previous findings published by the writer (1937-38) that allowing the land to lie fallow during summer season, so as to permit the washed soluble nutrients to return to surface soil to feed the plant, is far better than any manuring on the land under continuous irrigation.

These findings suggest that alluvial soils are sensitive to excess of irrigation. No sooner the plant nutrients are washed down in the lower stratum the land should receive no more irrigation. Judicious irrigation for maintenance of higher level of soil fertility is essential.

The use of soil solution methods helps greatly in the determination of soil nutrient values preparatory to prescribing profitable manurial treatments. The methods, however, have to be standardised for individual tracts.

(f) FIELD TESTS

As mentioned in the previous work by the writer (1939) definite corelation between the composition of soil solution and crop yield is established. Water or hydrochloric acid extraction methods could not throw any light on the immediate productivity of the soil. Data presented here (vide Tables I to IV) for different types of soils strengthen those findings ; in addition, it is observed that the chemical changes as occurring under field conditions are comparable with those taking place in the lysimeters. The results are shown in Table VI b.

Referring to the examination of saline and alkaline soils at different dynamical stages, under natural field conditions application of these methods have proved to be of great value.

Tamhane and Mulwani (1934) found that the liberal use of irrigation water improved the salt status of almost all saline soils in surface layers, whereas similar doses drained off valuable material from healthy soils.

However, study of movement of salts has something to do with the growing of crops having different root system at various stages of their growth.

Successful farming under conditions of salt and irrigation depends on controlling the movement of injurious salts so as to keep them away from feeding zone of crops. Following observations have been recorded in this connection.

On a piece of salt land measuring about an acre, cotton was doing well and first picking of seed cotton had just been taken. It was interesting to see white salt incrustations on the surface soil. The analyses of soil up to five feet depth gave the following salt distribution :—

Average of eight spots		
Layer	Total Salt (Soil soln..) %	Ca: Na ratio
0″-6″	1.55	0.12
6″-12″	0.64	1.10
12″-24″	0.58	2.20
24″-36″	0.36	2.80
36″-48″	0.25	3.40
48″-60″	0.22	3.80

Half the portion of this area was irrigated with eight acre inches of water in two doses with a view to get rid of the salts. Unfortunately 95% plants died on the irrigated portion whereas the plants on the unirrigated portion continued to thrive up till the usual third picking of cotton. The salt status of the irrigated land was as under :—

Average of eight spots		
Layer	Total salt (Soil soln.) %	Ca : Na ratio
0″6″	0.20	4.00
6″-12″	0.24	3.80
12″-24″	0.48	2.80
24″-36″	0.65	1.10
36″-48″	0.82	0.84
48″-60″	1.47	0.16

› It is therefore clear that salts were driven down to the feeding zone of the crop which is usually below 2 or 3 feet. The whole crop was damaged in addition to wastage of water. This salt status is however desirable at sowing time when the germinating seed needs least amount of toxic salts in the surface soil.

Similar observations were recorded by Webster and Viswanath (1921) in Iraq.

VI. DISCUSSIONS

The principal objects of the investigation were to make a preliminary inquiry into the soluble salt status of alkaline and non-alkaline soils in relation to irrigation practice as carried out in arid or semi-arid regions ; and to examine several changes that occur in such soils by observations of the displaced soil solution. Very little data is available as to the composition of soil solutions from such areas. Previous work by the writer and the recent work on some of the Indian soils as described in the foregoing pages manifest that it is not valid to assume in all cases that an aqueous extract of soil in whatever soil water ratio represents the liquid round about the soil particle under natural conditions. Viswanath (1939) and McGeorge (1937) have further strengthened the writer's observations that the methods of base exchange and pH determination now agreed upon as international ones are not applied to soil conditions at low moisture content Considerable discrepancies occur between the amounts of soluble and exchangeable matter, in all types of soils, determined by means of water extracts and those by displaced soil solution methods. Various reactions due to irrigation and common alkali salts on soils with different soil water ratios have been discussed and explained in foregoing pages. Conclusively, the divergence between the composition of soil solution and corresponding water extracts is a matter of great importance if the values obtained are assumed to represent the actual soluble salt status of soils at the time of examination.

Examination of soil water under field conditions in arid regions showed that under no circumstances the water content of the soil rises above 20 per cent. This represents one fifth of the soil weight. Whereas in 1 : 5 soil water extraction, the water is five times which means twenty-five times higher than the maximum soil water under irrigation conditions. Soil solution is, however, soil water displaced from a soil having 20% or less moisture content which is comparable with ordinary soils under cultivation. Soil solution therefore gives the most reliable information in all types of soils and evidently represents true liquid phase in soils and also forms the correct nutrient medium of crop. On the other hand the safe limits used in practice of water extracts are purely empirical and their application to different soils is of doubtful value. The practice of water extract may, however, be followed in case of very extensive surveys, over millions of acres, where millions of soil samples are tested with regard to total salinity without any consideration of real status of individual soil. The water extract method probably gives information from which a forecast of the effects of leaching can be deduced.

Three sizes of lysimeters were examined. The biggest, i.e., three feet drain pipe size appeared to be the most satisfactory and the results (vide

table VII) were comparable with those obtained under normal field conditions.

In the light of the experiments described, the use of proper size lysimeter tests, coupled with examination of the soil solution before and after irrigation, seems to offer a more reliable means of investigating the salt status of soil and the influence of irrigation both on salt affected and healthy soils.

Leaching experiments (Mulwani 1936) with the salted Devon soil .ulfilled expectation in that the bases displaced by salt additions were readily removed, and further with prolonged leaching far in excess of amounts used in practical irrigation, aluminium, iron, manganese and organic matter in considerable amounts appear in the drainage water, the proportions being larger in the case of salted soils. These values imply a more severe break down of the soil complex and probably of organic matter also. Leachings of salted Devon and naturally saline soils of Sind with the smaller amounts of water customary in irrigation indicate that under those conditions such changes do not take place.

Examination of leachings from lysimeter studies under conditions comparable with normal irrigation practice, indicate the same but less extensive changes. Removal of all constituents was increased by the salt treatment, and there was a tendency even in this case for a small increase in the organic matter in the leachings It should be noted that the soil used contained abnormally large amounts of ammonia and the values shown for this constituent must not be regarded as normal. Phosphates appeared in the second leaching, although the removal of Na and Ca at this stage could not have been very high.

Leaching with salt water produced similar general effects Changes in this case are delayed because the existing soil solution must be removed first. This probably constitutes the greater part of the first leachate. The rate of increase in concentration of successive leachate seems to indicate a somewhat slower displacement of K than Ca and Mg.

Soil solutions from the surface soils in which the leaching effects would be most apparent show very small proportions of nearly all constituents. Values for Ca and K are smaller in the salted than in the normal soil as is to be anticipated and the appearance of Fe and Al in salted sample suggest the beginning of break down of the complex.

Use of salt leaching water has effected a slightly more complete removal of Ca but a less efficient removal of Mg and K The case of replaceability is in the customary descending order, Ca, Mg, K.

In general, therefore, the action of salt in these experiments shows no exception to the general ideas of base-exchange phenomena.

In the ordinary course of the irrigation, the leaching process is followed by a steady rise of the sub-soil water towards the surface during the dry period.

In the lysimeters this return flow of water effects a redistribution in the proportion of Ca, Mg, Na, and K in soil solution as shown in Table XX.

Capillary rise of water through the control soil has resulted in an increase in the proportion of Ca, Mg, Na, and K in the surface soil solution and decrease in PO_4. In the case of Ca, Na, and Mg this probably represents merely the introduction of a new concentration gradient (high towards surface) naturally to be expected under these conditions ; the variations in concentration with depth being centred around a value of the same order as that in the original soil, and with the possible exception of Mg, without appreciable change in the total amounts of the individual bases appearing in the soil solution of the combined section. The gradation of the concentration indicates a rapidity of movement in the order Ca, Mg, Na (the order of ionic mobilities). In the case of K values at all depths exceed the origin al but the concentration gradient is in reverse order.

Similar conditions prevail in the case of salted soil except that in this the K gradient now conforms to that of the other bases and that the total amounts of Mg, Ca and Na in the combined sections fall short of those originally present. This is not true of K As before the clearance of bases is followed by increase in Po_4 concentration in the lower layers. Upward movement of salt solution through soil brings changes of similar character (K again falling into line with the other bases) although the major effect has not reached far beyond the middle section. The total amounts of water passing upward in the three pipes are not very different, and are of a similar order to the amounts of drainage water which appear after the usual irrigation dosage.

In considering the Sind soils it must be remembered that although all are of very similar type and mechanical composition (notably B and C) it is unsafe to make too close a comparison of the actual concentration in extracts and soil solutions. This was possible in the previous experiments where the identical soil was used throughout.

The composition of the soil solution from the three soils (known to increase in salinity in the order A, B, C) reflects the same relative base concentration as were produced by addition of salt to the Devon soil, viz , markedly higher values for Mg, Na and K, less difference in the case of Ca. Phosphate values are low in all these soils. The proportion of alkali carbonates lowers as salinity increases. The pH values of the soils are in qualitative agreement with the difference in alkali carbonate content. The leachings from these soils show the removal of soil constituents to be of the same qualitative nature as those observed in the salted Devon soils. There is the same general trend in the base ratios in successive leachings and the same qualitative order of difference between these ratios for the leaching of salt and normal soils in each case.

The effects of leachings as shown by the soil solution data of leached soils is again similar to that in the case of Devon soils. In all soils the depletion of Na and Mg is relatively greater than that of Ca and K. In Sind alkali carbonates are removed more effectively than alkaline earth carbonates from the Sind soils. (No observations of this were made in the Devon soils.)

The upward movement of fresh water through Sind soils again shows a number of characteristics similar to those of Devon soils.

In all three Sind soils the upward movement of water has induced an upward concentration gradient of the bases in the soil solution. In soil B, which resembles soil C more closely than does soil A there appears, the same general characteristics as in the unsalted Devon soil, viz., the mean values for separate bases tending to approximate to that of the original soil, indicating a shift of depth distribution rather than any notable change in base exchange equilibrium. It is notable that the K gradient is similar to that of other bases in all these soils. The reverse gradient in one case of Devon soils appears to be the outcome of exceptional and unperceived conditions. In soil C, as in the salted Devon soil, the sum total of Ca, Mg, Na, in soil solutions from the three layers is definitely less than that originally present. In the case of K values in all three layers are definitely above the original. Upward penetration of saline water through Sind soils A and B again effects changes comparable with those occurring in Devon soils. Changes in constituents due to upward movement in this case also appear to have proceeded nearer to the surface in the case of the more saline soil B.

Other effects (for which no comparable data for Devon soils are available) of the capillary rise of water and saline solution through the Sind soils are discussed in the foregoing pages.

Downward movement and leaching rate of water is discussed in saline and healthy soils.

The soil solution and the lysimetric technique have further been linked up with pot-culture trials on wheat. Definite relationship between soil solution results and soil productivity, so far as wheat performance is concerned, is established. Harmful effects of excess of irrigation by way of leaching have been demonstrated in case of normal soil which loses its nutrients in drainage No manurial treatment satisfactorily restores this lost fertility Return of drained out nutrients however recuperate the lost productivity These trials suggest judicious use of irrigation waters in the maintenance of higher level of soil fertility. They also assist in the determination of soil nutrient values preparatory to prescribing profitable manurial treatments. The methods have to be throughly standardized to meet individual requirements for different tracts.

Effects of water on healthy and salt affected soils have been studied under field conditions with regard to soil productivity and reclamation respectively.

Under salt and irrigation conditions movement of injurious salts should be controlled so as to keep the feeding zone free of salinity. In case of shallow rooting crops the salt should be driven down deep in lower layers, whereas in case of deep rooting crops the lower feeding zone should be kept devoid of harmful substances

VII. SUMMARY AND PRACTICAL ASPECT OF THE PROBLEM

In irrigated tracts there are already considerable areas of salt affected or otherwise poor lands. Still large areas are becoming increasingly saline and poor. It becomes necessary therefore to increase our know-

ledge of these soils, so as to gain such experience of them as will enable us to give definitely accurate information as to their suitability for any contemplated irrigation project. Partly in response to this need of such information this work was undertaken.

Technically there has been a general criticism, that in our agronomical work little or no use has been made of soil analysis firstly to determine the relationship of crop yield to the nature and amount of nutrients in the soil, secondly to make a basis for rational manuring.

It appears that the old methods of chemical analysis where use of large amounts of water, salt solution or acid is resorted to, do not give real reactive part of nutrient. Some drastic reactions occur in soil on addition of salt solution, acid or large doses of water.

The soil solution results as presented in the foregoing pages have thrown sufficient light on these and many other questions regarding soil fertility and alkalinity.

Study of soil water under natural conditions have elucidated that the soil solution methods do not require any excess of water over these conditions. Burd and Martin (1931) have also stated that the displaced soil solution which involves no excess of water represents the only precise measure of soil fertility.

The new lysimetric technique developed by the writer for the examination of salt and water movements and their effects on soils has shown to contribute extensively to the solution of problems likely to arise in connection with any irrigation scheme. Much depends on the use of correct technique of obtaining soil solution, and on the employment of suitable methods of analysis, which are naturally on a "micro" scale.

On this basis the use of soil solutions has been made in the examination of many chemical changes in soil, of the depth-distribution and movement of soluble constituents, which would have been impossible with water or acid extracts.

Van Wijk (1929) in Pretoria confirmed that an ordinary aqueous extract of a soil is not going to throw much light on the actual concentration of the soil solution.

The results obtained under the investigation entitled, "Salt and irrigation" are summarised below :—

(1) Treatment of normal English soil, with varying proportions of Nacl produced, increases in the base contents of displaced soil solution in accordance with accepted theories of base exchange. The increase in Mg concentration was unexpectedly high. Fe, Al, and Mn were brought into solution by this treatment in soil of low $CaCO_3$ reserve and phosphates disappeared from the soil solution. Fixation of phosphorus under these conditions is probably not associated with Al or with pH.

(2) Leaching of these soils with amounts of water comparable to those used in irrigation practice, resulted in the anticipated removal of bases (to greater extents in said soils) of Al, PO_4 and NO_3.

Soil solutions from leached soils showed considerable depletion of all bases (more severe in the case of Mg and Na) a return of PO_4 from salted soil corresponding to the elimination of excessive bases and a slight increase in organic nitrogen, Fe and Al.

More prolonged leaching intensified all these effects.

(3) The capillary rise of water through soils cause a return of all bases towards the surface layers, and with rising concentration gradient towards the surface (one exceptional instance in the case of K is recorded). In the case of unsalted soil there seems little more than a new depth-distribution of the total base originally present in the soil. Upward movement of water through saline soil produces similar concentration gradients, but the total Mg, Ca, Na present in the solution from combined strata is less than the corresponding totals originally present. In case of K values, at all depths, exceed the original.

(4) Comparison of data referred to in (2) and (3) with corresponding data for natural saline soils from Sind reveals no fundamental difference between artificially salted and natural saline soils in these respects. Artificially salted soils, the salinity of which can be controlled with some accuracy, appear to be utilisable for experimental work dealing with irrigation problems in naturally saline soils.

(5) Leaching experiments with natural saline soils in small scale lysimeters and subsequent analysis of soil solutions taken from three different depths indicate that the leaching of bases previously referred to in (3) results in an increase in the ratio Ca : Na and Ca : Mg and a decrease in the Na : K ratio in the salt solution. This is regarded as an improved base status. On the other hand in a non-saline soil of similar type leaching tends to produce adverse effects at depths greater than ten inches in which the Ca : Na ratio appears to decrease.

The Na_2Co_3 contents of the soil solution is decreased in all cases.

(6) The capillary rise of water and of former leachates through soils is also examined by lysimeters. Upward penetration of water appears to proceed in advance of changes in base ratios resulting from it The observed changes in base contents of the soil solution indicate a pronounced tendency to improve the Ca : Na ratio which is more marked in the upper layers of saline soil and in the lower layers of the sweet soil. In all cases there is a notable decrease in the Na_2CO_3 content at all depths. The decrease in the alkaline earth carbonates is less marked in the saline soil. Upward seepage of saline leachate through a normal soil causes marked increases in the concentration of all solutes in the soil solution. In these experiments in which further upward movement would still have been possible this increase was apparent to within ten inches of the surface. Ca : Na and Ca : Mg ratios tended to decline to a considerable extent and the Na: K ratio to increase.

These results indicate that upward seepage of drainage water through soils from which it has been derived produces no very harmful results, and in some cases slight improvement may result. Seepage of saline drainage water upward through a normal healthy soil may produce in it conditions approximating to a definitely harmful salinity.

When the upward seepage is more prolonged (equivalent approximately to that obtainable from a doubled irrigation dosage) the passage of fresh water through a non-saline soil causes nearly a sharp concentration gradient towards the surface without serious change in the base ratios. The prolonged upward movement of saline water through a non-saline soil leads to increased concentration of all soil solution constituents. These increases appear to reach a maximum at sub-surface depths (8-15 inches). Chloride seems to penetrate to a greater extent into the surface layers than into the bases. Under these conditions the surface measure retains approximately the same base ratios in the soil solution as in the original but there is a rapid and serious deterioration with depth.

Prolonged upward movement of water through partially saline soils increases the concentration gradient of solutes towards the surface without very great changes in base values. There is a definitely lower Na_2CO_3 concentration at all depths.

In soils of high salinity similar changes occur but in this case the base ratios in the upper layers are adversely affected.

More extended capillary use of saline water through a partially saline soil serves merely to intensify its originally unsuitable conditions.

By use of small lysimeters permitting detachment of their contents in a number of separate layers, changes in the composition of soil solution and the movement of its mineral constituents resulting from irrigation and from the upward movement of water are examined. The bearing of these observations on certain irrigation problems is discussed.

This preliminary investigation evidently indicates the satisfactory nature of soil solution methods, and of the small scale lysimeter technique in the examination of soluble salt movements in soils.

The soil solution and lysimetric technique have further been linked up with pot culture trials on wheat. Definite relationship between soil solution results and soil productivity, so far as wheat performance is concerned is established. Harmful effects of excess of irrigation by way of leaching have been demonstrated in case of normal soil which loses its nutrients in drainage. These trials suggest judicious use of irrigation waters in the maintenance of high level of soil fertility. The methods assist in determining soil nutrient values preparatory to prescribing profitable manuring. Recently White and Ross (1939) have studied the effects of various fertilizers on soil solution of different types of soils.

Effects of water on healthy and salt affected soils have been studied under field conditions with regard to productivity and reclamation respectively.

General principles followed in the management of irrigated soils :—

Liberal use of irrigation water improves the salt status of almost all saline soils in surface layer, whereas such heavy doses drain off valuable material from healthy soils. However, study of movement of salts has something to do with the profitable crop growing. Successful farming

under conditions of salt and irrigation depends on controlling the move-
ment of injurious salts so as to keep them away from feeding zone of
crops. In case of shallow rooting crops the salt should be driven down
deep in lower layers, whereas in case of deep rooting crops the lower
feeding zone should be kept free from harmful substances. In the latter
case no attempt should be made to wash down the salts if seen on the
surface.

In general following principles should be observed :—

(1)   The movement of water in the soil must be controlled as rigidly
as possible.

(2)   When land is irrigated no more water than is absolutely necessary
for the plants should be used.

(3)   Worst salt affected patches located by means of soil survey should
carefully be kept out from irrigation system if there is more land than
can possibly be irrigated.

(4)   Drainage water from the irrigated land should not be allowed to
wander where it will, but led to some definite place where it can do no
harm to the main area.

VII (a). ABSTRACT

(1)   A detailed inquiry into the soluble salt status of alkaline and
non-alkaline (healthy) soils in relation to irrigation practices has been
made.

By use of small scale lysimeters permitting detachment of their contents
in a number of separate layers, changes in the composition of soil solution
and the movement of its mineral constituents resulting from irrigation
and from the upward movement of waters are examined. The technique
developed has shown to contribute extensively to the solution of problems
likely to arise in connexion with irrigation practices.

(2)   It is found that the addition of sodium chloride to soils results
in (a) a depression of the solubility of phosphates, the action being
reversible when sodium chloride is removed by irrigation, drainage,
etc., (b) movement of organic nitrogen constituents which thus become
capable of upward and downward movement in the soil, (c) movement
of iron, aluminium, manganese, in soils of low but not in those of high
lime content.

(3)   Examination of leachings, and soil solution from artificial and
natural saline soils under various conditions show a general similarity of
all characteristics examined. Use of artificially salted soils, therefore,
appears to offer a reliable experimental basis for investigation of problems
concerned notably with irrigation of saline soils.

(4)   Comparison is made of the composition of displaced soil solution
and that of corresponding water extracts in which the soil water ratio
is varied. Soil extracts are shown to indicate much larger proportion
of soluble calcium, potassium, carbonate, phosphate, and higher calcium
sodium ratio (on dry soil basis) than actually appear in the soil solution.
The use of water extracts in assessing the proportion of soil fertility

ingredients or harmful soluble salts (in case of saline soils) seems somewhat unsatisfactory.

(5) Liberal use of irrigation water improves the salt status of almost all saline soils in surface layers, whereas such heavy doses drain off available plant food material from healthy soils. In case of salt free healthy soils, judicious and economical use of irrigation water is recommended for maintenance of high level of soil fertility.

(6) The new methods assist in the determination of soil nutrient values preparatory to prescribing profitable manurial treatments.

VIII. STANDARDIZATION OF THE METHODS

The author is convinced of the value of soil solution methods in fundamental investigation of several irrigation problems and expects them to be of universal application. Those who are acquainted with the practical aspects of irrigational problems will select vital points which are best calculated to yield information on submission to these methods.

It is, however, suggested that the methods be thoroughly standardized and modified in different countries to work out individual problems.

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APPENDIX

TABLE I

Composition of soil solution and water extract from healthy Sind soil

(Figures expressed as p. p. m on dry soil)

Soil Water		Ca	Mg	Na	K	PO$_4$	pH	Ca : Na ratio	Ca : Mg ratio	Na : K ratio
Soil solution	..	150	30	30	40	0.3	7.2	5	5	0.75
1 :5 extt	..	200	35	35	30	4.0	7.6	6.66	5.7	0.6

TABLE II

Soil solution and water extracts of Sind Alkaline soils

Soil Type	Soil: Water ratio	Total soluble matter %	Ca %	Mg %	Na %	K %	Na$_2$CO$_3$ %	PO$_4$ p. p. m	Ca : Na ratio	Ca : Mg ratio	Na : K ratio	pH
Slightly Alkaline	Soil Soln.	1.837	0.0124	0.0118	0.389	0.0298	0.0212	0.4	0.03	1.05	13.06	9.2
	1:1 extt	2.567	0.0427	0.0124	0.406	0.0388	0.0034	0.4	0.105	3.44	10.5	8.9
	1:5 extt	3.254	0.2596	0.0216	0.396	0.0578	Nil	2.0	0.65	12.02	6.9	7.5
Alkaline	Soil Soln	2.502	0.0105	0.0120	0.428	0.0318	0.164	Traces	0.02	0.97	13.5	6.8
	1:1 extt	2.522	0.0220	0.0125	0.402	0.0444	0.0401	0.2	0.05	1.76	9.1	9.1
	1:5 extt	3.252	0.2284	0.0202	0.390	0.0892	Nil	2.2	0.58	11.30	4.4	7.6

TABLE III
Punjab Alkaline Soils

Punjab-soils	Soil: Water ratio	Total salt %	Ca %	Mg %	Na %	K %	NaCO₃ %	PO₄ p.p.m.	Ca:Na ratio	Ca:Mg ratio	Na:K ratio	pH
Bara Farm Montgomery	Soil soln.	1.23	0.01	0.012	0.51	0.09	0.25	Nil	0.02	0.83	5.7	9.9
	1:1 extt.	1.81	0.052	0.034	0.58	0.12	0.21	T	0.09	1.53	4.8	9.5
	1:5 extt.	1.95	0.11	0.021	0.50	0.17	0.17	0.5	0.22	5.24	2.9	9.2
Alkali lands Muzaffarabad Multan	Soil soln.	1.17	0.01	0.013	0.33	.08	0.44	Nil	0.03	0.77	4.1	9.9
	1:1 extt.	1.52	0.06	0.045	0.54	0.14	0.32	T	0.1	1.33	3.9	9.4
	1:5 extt.	1.78	0.12	0.02	0.43	0.16	0.28	0.5	0.25	6.00	3.0	9.1
Alkali land * Sahiwal, Sheakpur	Soil soln.	1.35	0.03	0.029	0.30	0.03	0.49	Nil	0.10	1.03	10.0	9.0
	1:1 extt.	1.67	0.08	0.026	0.32	0.04	3.31	0.2	0.25	3.08	8.0	8.5
	1:5 extt.	1.93	0.25	0.026	0.40	0.06	0.25	1.8	0.62	9.61	6.6	8.2

It is seen that pH values are correlated with Ca : Na ratios and Na₂CO₃ amounts.

T= Traces

TABLE IV
Composition of soil solution and water extracts of Delhi soil
Figures expressed as p. p. m. on dry soil

Soil: Water ratio	Ca	Mg	K	Na	Cl	SO₄	HCO₃	PO₄	Ca:Na ratio	Ca:Mg ratio	Na:K ratio
Soil Soln	42	9	1.5	40	187	28	5	0.5	1.02	4.7	26.66
1:1 extt.	45	4	6	45	90	18	30	2	1.0	11.25	7.5
1:5 extt.	131	15	11	10	162	412	75	6	13.1	8.7	.9

TABLE IV (a)

Effect of different amounts of Sodium salts on Delhi soils at different soil water ratios

p. p. m.

Soil Treatment	Soil : Water ratio	Ca	Mg	Na	K	Cl	SO₄	HCO₃	Na₂CO₃	Ca/Na	Ca/Mg
0.1%	Soil Soln.	199	20	371	10	803	35	8	...	0.5	9.9
	1:1 Extt.	131	17	400	Nil	601	268	23	...	0.3	7.7
	1:5 Extt.	102	18	400	T	600	927	113	...	0.2	5.6
NaCl 0.5%	Soil Soln.	455	43	1680	24	2850	22	3	...	0.2	16.5
	1:1 Extt.	229	19	1650	Nil	2440	309	23	...	0.1	12.0
	1:5 Extt.	194	..	1650	T	2325	412	113	...	0.1	..
NaCl 1.0%	Soil Soln.	552	54	2700	23	5247	10	3	...	0.2	10.2
	1:1 Extt.	315	24	3300	Nil	4600	10	23	...	0.09	13.1
	1:5 Extt.	295	24	4000	T	4600	824	75	...	0.07	12.2
Na₂SO₄ (Equivalent of 0.1% Nacl)	Soil Soln.	68	..	250	3.4	190	324	5	...	0.2	..
	1:1 Extt.	110	32	160	T	110	577	23	...	0.6	34.8
	1:5 Extt.	164	12	300	T	150	803	75	...	0.5	13.6
Na₂SO₄ (Equivalent of 0.5% Nacl)	Soil Soln.	59	18	960	T	198	2123	37	...	0.6	3.2
	1:1 Extt.	348	24	700	2	170	3226	23	...	0.5	14.5
	1:5 Extt.	286	18	2000	T	150	4550	75	...	0.1	15.8
Na₂SO₄ (Equivalent of 1.0% Nacl)	Soil Soln.	65	29	2260	9	198	4780	14	...	0.2	2.2
	1:1 Extt.	434	27	2250	5	170	5427	23	...	0.1	16.0
	1:5 Extt.	317	18	3600	T	150	7159	75	...	0.8	17.6
Na₂CO₃ (Equivalent of 0-1% Nacl)	Soil Soln.	29	2	275	T	175	Nil.	31	..	0.1	14.5
	1:1 Extt.	18	..	20	T	140	391	75	..	0.9	..
	1:5 Extt.	53	..	250	T	150	618	225	348	0.2	..
Na₂CO₃ (Equivalent of 0.5% Nacl)	Soil Soln.	18	1	1160	T	246	48	150	162	0.01	18.0
	1:1 Extt.	24	..	225	T	100	350	300	810	0.1	..
	1:5 Extt.	94	..	1009	T	150	..	1050	3400	-0.09	..
Na₂CO₃ (Equivalent of 1.0% Nacl)	Soil Soln.	10	2	1768	22	313	68	540	2052	0.04	5.9
	1:1 Extt.	33	..	T	85	200	Nil.	1500	2970	..	..
	1:5 Extt.	78	..	2000	6	225	Nil.	1950	...	0.03	..

TABLE IV (b)

Effect of different amounts of Calcium salts on Delhi soil at different soil water ratios

Parts per Million

Salt Treatment	Soil : Water ratio	Ca	Mg	Na	K	Cl	SO₄	HCO₃	Ca Na	Ca Mg
CaCl₂ 0.1%	Soil Soln	383	29	57	15	774	15	8	6.7	13.2
equivalent of NaCl	1:1 Extt.	160	17	320	5	280	247	15	0.5	9.4
	1:5 Extt.	286	18	110	T	500	1751	75	2.6	15.8
Ca₂Cl₂ 0.5%	Soil Soln.	1355	45	53	23	2508	16	6	25.5	30.1
equivalent of NaCl	1:1 Extt.	474	19	320	5	680	247	15	1.4	24.9
	1:5 Extt.	1043	36	85	T	2025	824	40	1.2	29.0
CaCl₂ 1.0%	Soil Soln.	2461	50	50	17	4496	16	3	45.2	49.2
equivalent of NaCl	1:1 Extt.	1423	24	480	13	2100	247	23	3.0	59.2
	1:5 Extt.	1718	42	85	T	3250	569	40	20.2	40.9
CaSO₄ 0.1%	Soil Soln.	155	12	34	5	179	199	17	4.5	12.9
equivalent of NaCl	1:1 Extt	213	17	300	2	110	845	23	0.7	12.5
	1:5 Extt.	335	18	100	25	125	2112	40	3.3	18.6
CaSO₄ 0.5%	Soil Soln	133	11	32	5	158	201	15	4.1	12.0
equivalent of NaCl	1:1 Extt	654	19	240	2	70	1483	23	2.7	34.4
	1:5 Extt	992	39	60	16	50	3605	40	16.5	25.4
CaSO₄ 1.0%	Soil Soln.	140	11	30	3	163	214	8	4.6	12.7
equivalent of NaCl	1:1 Extt.	663	17	240	T	60	1007	23	2.7	39.9
	1:5 Extt	2147	48	125	7	100	6438	40	17.1	44.7
CaCO₃ 0.1%	Soil Soln.	87	7	40	4	212	56	3	2.1	12.4
equivalent of NaCl	1:1 Extt.	90	12	320	9	160	124	30	0.2	7.5
	1:5 Extt.	131	24	105	18	175	N64.	130	1.2	5.4
CaCO₃ 0.5%	Soil Soln.	69	5	34	4	154	35	17	2.0	13.8
equivalent of NaCl	1:1 Extt.	90	10	260	3	115	206	30	0.3	9.0
	1:5 Extt.	106	15	75	18	150	20	75	1.4	7.0
CaCO₃ 1.0%	Soil Soln.	65	5	30	4	158	36	8	2.1	13.0
equivalent of NaCl	1:1 Extt.	90	7	320	4	100	124	30	0.2	12.5
	1:5 Extt.	143	15	12	18	150	462	113	11.9	9.5

TABLE IV(o)

Effect of common Alkali salts with and without Calcium salts (Delhi Soil)

Parts per Million

Soil Treatment Common Salts of Alkali	Soil-Water	Ca	Mg	Na	K	Cl	SO_4	HCO_3	Na_2CO_3	Ca/Na	Ca/Mg
(I)											
Artificially salted (with Ca Salts)											
$CaCO_3$ 2.5%	Soil Soln.	133	123	1830	239	2431	3309	6	72	0.07	1.0
$CaSO_4$ 0.5%	1:1 Extt.	487	53	800	138	900	2802	15	Nil	0.6	9.1
NaCl 0.5%	1:5 Extt.	941	157	2000	192	2200	6386	75	Nil	0.5	6.0
Na_2SO_4 0.5%											
Na_2CO_3 0.1%											
$MgSO_4$ 0.5%											
K_2SO_4 0.2%											
(II)											
Artificially salted (without Ca and Salts)											
NaCl 0.5%	Soil Soln	113	180	3075	15	2770	2906	8	144	0.03	0.6
Na_2SO_4 0.5%	1:1 Extt.	266	87	1300	T	1760	2245	38	Nil	0.2	3.0
Na_2CO_3 0.1%	1:5 Extt	429	133	4000	21	2600	4996	113	Nil	0.1	3.2
$MgSO_4$ 0.5%											

TABLE IV(d)

Calculated amounts of ions added to soils under different salt treatments vide Tables IV a to o

Parts per Million

		Ca	Mg	Na	K	CO₃	SO₄	Cl.
NaCl	0.1	...	...	390	...	...	...	590
,,	0.5	...	...	1950	...	...	...	2900
,,	1.0	...	...	3900	...	...	...	5800
Na₂SO₄	0.1	...	...	390	...	...	830	...
,,	0.5	...	...	1950	...	...	4150	...
,,	1.0	...	...	3900	...	...	8300	...
Na₂CO₃	0.1	...	...	390	...	520	...	...
,,	0.5	...	...	1950	...	2960	...	...
,,	1.0	...	...	3900	...	5200	...	...
CaCl₂	0.1	341	...	...	...	...	...	614
,,	0.5	1705	...	...	...	...	...	3070
,,	1.0	3410	4	...	...	...	...	6140
CaSO₄	0.1	341	...	...	...	...	835	...
,,	0.5	1705	...	...	...	...	4175	...
,,	1.0	3410	...	...	...	...	8350	...
CaCO₃	0.1	341	...	...	...	510	...	...
,,	0.5	1705	...	...	...	2550	...	...
,,	1.0	3410	...	...	...	5100	...	...
Mixture of common salts of Alkali soils with calcium 11500	...	1500 Soluble 10000 insoluble	1000	3980	440	15570	12600	3000
Mixture of common salts of Alkali soils without calcium	...	Nil.	1000	3980	....	570	7400	3000

TABLE V

Moisture per cent. in a virgin plot at Sakrand, Sind, before and after irrigation

Figures are rounded up

Soil Layer	Before irrigation (Summer) 1-8-1938	Before irrigation (Winter) 1-1-139	After 6 inches irrigation 10-1-1939
0'—1'	2	2	14
1'—2'	2	2	19
2'—3'	2	5	19
3'—4'	4	7	18
4'—5'	8	8	16
5'—6'	11	11	11
6'—7'	12	12	12
7'—8'	12	16	17
8'—9'	16	20	20
9'—10'	18	17	18
10'—11'	16	13	13
11'—12'	19	18	18

Note.—Sub-soil water level was situated at about 20 feet below surface.

TABLE VI

Results of analyses as obtained by different sizes of miniature lysimeters

Alkali—Saline Soil

Figures expressed in p.p.m. on dry soils

Lysimeter	Leachate Volume	Ca	Na	K	PO$_4$	Na$_2$CO$_3$	Na Ca ratio	pH	Time taken to collect one litre (Hours)
Bottle size	I litre	0.45	0.81	0.16	0.8	0.03	0.56	8.4	125
	II litre	0.25	0.50	0.12	1.4	0.01	0.50	8.2	107
	III litre	0.05	0.19	0.08	1.4	Nil	0.25	8.0	340
	Average	0.25	0.50	0.12	1.2	0.01	0.50	8.2	
One foot Drain pipe	I litre	0.08	0.82	0.10	T	0.08	0.10	9.4	26
	II litre	0.06	0.56	0.08	0.2	0.06	0.10	9.2	47
	III litre	0.04	0.30	0.06	0.3	0.03	0.13	8.4	91
	Average	0.06	0.56	0.08	0.2	0.06	0.11	9.0	
Three feet Drain pipe	I litre	0.013	0.65	0.042	Nil	0.12	0.02	9.9	16
	II litre	0.012	0.53	0.041	Nil	0.11	0.02	9.8	21
	III litre	0.011	0.35	0.041	T	0.11	0.03	9.6	29
	Average	0.012	0.51	0.04	Nil	0.11	0.02	9.8	
Displaced soil solution and water extracts of same soil	Soil soln.	0.011	0.52	0.04	Nil	0.12	0.02	9.7	
	1:1 Extt.	0.07	0.58	0.08	0.3	0.06	0.12	9.1	
	1:5 Extt.	0.28	0.56	0.11	1.4	0.01	0.41	8.3	

TABLE VI(a)

Results of analyses as obtained by different sizes of miniature lysimeters

Normal healthy soil

Figures expressed in p.p.m. on dry soils

Lysimeter	Leachate Volume		Ca	Na	K	PO$_4$	Na$_2$CO$_3$	Na : Ca ratio	pH	"Hours" Time taken to collect one litre.
Bottle size	I litre	..	0.031	0.008	0.008	2.5	*Nil*	4	7.3	245
	II litre	..	0.021	0.007	0.006	3.5	*Nil*	3	7.5	284
	III litre	..	0.014	0.007	0.006	3.0	*Nil*	3	7.5	315
	Average	..	0.022	0.007	0.006	3.0	*Nil*	3.1		
One foot Drain pipe	I litre	..	0.024	0.006	0.006	0.9	T	4	7.4	42
	II litre	..	0.018	0.006	0.005	1.1	T	3	7.5	45
	III litre	..	0.015	0.005	0.005	1.1	T	3	7.5	48
	Average	..	0.019	0.006	0.005	1.0	T	3.2		
Three feet Drain pipe	I litre	..	0.016	0.003	0.004	0.4	0.001	5.3	7.3	28
	II litre	..	0.015	0.003	0.004	0.4	0.001	5.9	7.3	24
	III litre	..	0.015	0.003	0.004	0.4	0.001	5.0	7.3	28
	Average	..	0.015	0.003	0.004	0.4	0.001	5.0		
Displaced soil solution and water extracts of same soil	Soil soln. 1:1 Extt.	..	0.014	0.003	0.004	0.3	0.001	4.7	7.3	
			0.018	0.005	0.005	1.5	T	3.6	7.5	
	1:5 Extt.	..	0.023	0.007	0.007	3.2	Nil	3.3	7.5	

TABLE VI (b)

Soil changes occurring after six inches irrigation under natural conditions and under lysimeter technique

Soil depth	Plot soil						Drain pipe soil					
	Total soluble matter %	Ca %	Mg %	Na %	K %	pH	Total soluble matter %	Ca %	Mg %	Na %	K %	pH %
0'—1'	0.26	0.010	0.004	0.01	0.008	8.2	0.24	0.01	0.004	0.01	0.008	8.1
1'—2'	0.29	0.015	0.008	0.02	0.008	8.2	0.28	0.016	0.006	0.02	0.010	8.1
2'—3'	0.35	0.018	0.008	0.08	0.012	8.3	0.34	0.018	0.008	0.09	0.012	8.3
3'—4'	0.69	0.020	0.014	0.16	0.018	8.4	0.67	0.022	0.012	0.15	0.016	8.5
4'—5'	0.87	0.022	0.018	0.32	0.018	8.4	0.89	0.022	0.016	0.33	0.018	8.4

TABLE VII

Drainage waters in successive lots from three different treatments (Devon soil)

Results of Chemical Analyses "pH and p.p.m. ions" (on leachings)

Drainage water from different pipes	Nitrogen			Ca	Mg	K	Na	Cl	Al	PO$_4$	pH	Volumes of leachings c.c.
	NH$_3$	NO$_3$	org.									
Pipe No. 3												
Normal soil with distilled water—												
I. Leaching	75.0	50.0	128.8	242	81.9	54.2	134	319	2	2.8	4.8	325
II. do.	64.5	55.2	148.5	122	81.9	44.5	134	319	3	2.0	4.9	380
III. do.	46.5	41.0	182.0	84	85.8	40.5	126	248	3	2.0	5.1	300
Pipe No. 4												
Salted (1%) soil with distilled water—												
I. Leaching	120.0	62	196.7	1202	310.7	154.4	8010	17395	5	Nil	4.5	445
II. do.	127.5	41.5	202.0	1017	308.1	152.9	7800	17395	5	0.8	4.5	540
III. do.	153.0	46.0	186.5	1092	302.4	147.2	3538	3905	5	1.6	4.4	300
Pipe No. 5												
Normal soil with salt water—												
I. Leaching	55.5	73.5	221.0	272	79.3	74.3	189	497	2	2.4	4.9	350
II. do.	66.0	43.0	239.5	357	141.7	75.5	375	1065	4	2.2	4.8	360
III. do.	87.0	38.5	208.0	782	262.6	89.0	1115	3200	5	1.2	4.8	350

TABLE VIII

Soil solution after leaching

p.p.m. on oven-dry soil and pH

Leached soil	Nitrogen			Ca	Mg	Na	K	Fe	Al	PO	PH
	NH₃	NO₃	Org.								
Layers from different pipes Pipe No. 3. Normal soil distilled water Surface layer of soil	6.0	9.5	32.0	10.2	Nil	Nil	5.13	2.0	Nil	Nil	5.9
Pipe No. 4. Salted soil with distilled water Surface layer of soil	1.5	6.3	38.3	8.5	Nil	Nil	2.16	5.5	0.18	1.5	5.1
Pipe No. 5. Normal soil with salt water Surface layer	16.0	5.2	45.3	5.0	5.6	2289	13.2	1.5	0.43	0.2	5.3
Middle layer	48.0	6.3	51.2	11.5	24.6	2397	47.7	1.0	0.86	0.4	5.3
Bottom layer	87.0	6.5	63.8	71.7	147.2	2541	74.7	Nil	2.25	0.6	5.0

TABLE IX

Composition of soil solutions (Devon soil)

Influence of upward movement of fresh water through original and salted soil and of salt water through original soil

(p. p. m. on dry soil)

Capillary affected soil layers from different treatment	Nitrogen			Ca	Mg	Na	K	Fe	Al	PO$_4$	pH	Volume of water passed by capillary action c.c.
	NH$_3$	NO$_3$	Org.									
Pipe No. 6 (water through soil)												
Surface layer of soil	34.8	28.6	25.0	91.5	7.6	47.1	17.4	*nil*	0.15	0.4	6.0	850
Middle do.	30.0	18.5	32.0	10.5	3.9	39.0	19.8	*nil*	*nil*	0.2	5.5	
Lower do.	11.5	5.3	39.5	8.5	0.9	10.0	33.1	0.5	*nil*	0.2	6.1	
Pipe No. 7 (water through salted soil)												
Surface layer of soil	94.5	25.1	68.4	521.2	124.2	2879	70.7	*nil*	0.2	0.2	4.8	860
Middle do.	70.5	16.8	62.1	270.0	84.1	2520	52.8	*nil*	0.15	0.6	5.1	
Lower do.	18.2	4.9	40.9	*nil*	8.2	266	12.6	0.7	0.2	1.1	5.6	
Pipe No. 8 (salt water through soil)												
Surface layer of soil	29.7	22.1	49.0	8.0	17.9	57	21.5	1.5	0.15	0.4	5.6	890
Middle do.	58.8	14.1	98.8	60.0	67.8	470	39.0	*nil*	0.15	0.4	5.3	
Lower do.	56.6	3.2	85.4	138.0	46.8	4192	120.0	*nil*	0.4	0.2	5.3	
I Control (original soil) pipe 1	29.0	..	..	36.0	1.7	30.4	6.8	*nil*	1.7	1.96	5.9	
II Control (Salted Soil) pipe 2	93.0	..	..	398	344	2085	39.4	*nil*	52.4	*nil*	5.15	

TABLE X

Chemical composition of soil solution from the Sind soils

p. p. m. on oven-dry soil and pH

Soil type	pH	Ca	Mg	Na	K	PO$_4$	Total soluble salts	Chlorine	Soluble CO$_3$ other than Na$_2$CO$_3$	Na$_2$CO$_3$	Ca:Na ratio
A ..	7.6	101	17.7	25.3	22.66	0.24	616	66	53.9	11.0	4.0
B ..	7.7	187	40.1	231.7	45.54	0.13	1837	495	42.9	17.0	0.81
C ..	8.4	145	136.7	3820.0	275.50	0.21	12100	4374	23.4	63.4	0.04

N.B.—Al, Fe and Mn absent from all samples.

TABLE X(a)

Physical Composition

Soil type	Caly %	Silt %	Fine sand %	Coarse sand %	Ca CO$_3$ %
A	12.70	24.45	43.22	0.5	10.50
B	17.38	33.57	29.43	0.7	10.50
C	16.25	36.10	27.45	0.2	9.50

Nitrogen

	NH$_3$	NO$_3$	Org
A	0.4	6.2	2.4
B	0.4	8.8	0.8
C	1.1	125	0.5

TABLE XI

Sub-surface layers taken from the three types of plots—A. B. & C.

Layer	Plot A.		Plot B		Plot C.	
	F. Sand %	T. Salts %	F. Sand %	T. Salts %	F. Sand %	T. Salts %
1'—2'	43.8	0.06	24.1	0.95	26.4	1.53
2'—3'	63.4	0.06	22.0	0.38	14.6	1.56
3'—4'	56.6	0.09	33.1	0.76	34.3	0.58
4'—5'	47.8	0.16	60.1	0.20	22.0	0.78
5'—6'	51.5	0.17	23.5	0.38	25.4	1.06
Total	263.1	0.54	162.8	2.67	122.7	5.51
Average	52.6	0.11	32.6	0.53	22.5	1.10

TABLE XII

(1) Effect of artificial leaching on normal type of soil

SIND SOIL TYPE A

(Expressed as p. p. m. on leachate)

Leachate	Ca	Mg	Na	K	Cl	Soluble CO₃ other than Na₂CO₃	Total salts	Nitrate N	PO₄	Na₂Co₃	pH	Ca:Na ratio	Leachate volume c.c	Ca:Mg ratio	Na:k ratio
First	652	149.18	139	128	536	152	4580	12	0.4	44	8.2	4.7	150	4.4	1.1
Second	562	145.0	138	126	444	170	4300	6	0.1	34	8.0	4.1	150	3.9	1.1
Third	472	132.0	131	125	202	176	2240	1	0.1	29	7.9	3.6	150	3.6	1.0

SIND SOIL TYPE A

(Absolute quantities removed in leachates)

(Milligrams)

Leachate	Ca	Mg	Na	K	Cl	CO₃	Total salts	Nitrate N	PO₄	Na₂CO₅	Ca:Na ratio	Ca:Mg ratio	Na:K ratio
First	97.8	22.5	20.0	19.2	80.4	22.8	687.0	1.8	0.06	6.6	4.6	4.3	1.1
Second	84.3	21.8	20.7	18.9	66.6	23.5	645.0	0.9	0.01	5.1	4.1	3.9	1.1
Third	70.8	19.8	19.7	18.8	30.3	26.4	486.0	0.15	0.01	4.4	3.6	3.6	1.0

Table XIII (a.

(Leached Soil B p.p.m. on dry soil and pH)

Layer	Ca	Mg	Na	K	Cl	CO₃	Total salts	NO3 N	PO4	Na2 CO3	pH	Ca:Na	Ca:Mg	Na:K
Upper	119	15	10	19	29	20	706	1	0.05	1.9	8.2	11.9	7.9	0.5
Middle	104	28	52	34	49	16	893	2	0.05	2.3	8.0	2.0	3.7	1.6
Lower	93	38	198	40	57	30	1543	2	0.05	9.4	8.4	0.5	2.4	4.9
Original Soil	187	40	232	45.5	495	54	1837	8.8	0.13	17.0	7.7	0.81	4.6	4.2

Soil B: percentage of original values after leaching

Layer	Ca	Mg	Na	K	Cl	CO₃	Total salts	NO3 N	PO4	Na2CO3
First	04	37	4.3	11	6	37	37	11	38	12
Second	56	70	22.4	74	10	30	48.5	22	38	13
Third	50	95	85.0	87	11.05	55	84	22	38	55

TABLE XIV

(3) *Effect of artificial leaching on saline soil : (Sind Soil Type C)*

(Expressed as p.p.m. on leachate)

Leachate	Ca	Mg	Na	K	Cl	CO₃ (other than Na₂CO₃)	Total salts	Nitrate N	PO₄	Na₂CO₃	pH	Ca:Na	Ca:Mg	Na:K	Volume c.c.
First ..	756	741	18314	850	28045	140	78040	136	0.2	145	8.6	0.04	1.0	21.3	500
Second ..	718	700	16034	1740	16330	174	72180	111	0.1	216	8.8	0.04	1.0	9.2	250
Third ..	550	513	13205	1139	2278	210	49400	55	0.05	255	8.6	0.04	1.1	11.6	300

Sind Soil C: absolute quantities removed in leachates

m.g.m. (milligrams)

Leachate	Ca	Mg	Na	K	Cl	CO₃	Total Salts	NO₃ N	PO₄	Na₂CO₃	Ca:Na	Ca:Mg	Na:K
First ..	378	370	9157	425	14022	70	39020	63.0	0.1	72.5	0.04	1.0	21
Second ..	177	175	4008	435	4082	43	18045	27.7	0.02	54.0	0.04	1.0	9
Third ..	165	153	3962	341	683	63	14808	16.5	0.15	76.5	0.04	1.1	11

6 (a)

TABLE XIV(a)

(Leached soil C. p.p.m. on dry soil and pH)

Leached soil layer	Ca	Mg	Na	K	Cl	CO$_3$	Total salts	NO$_3$ N	PO$_4$	Na$_2$CO$_3$	pH	Ca:Na	Ca:Mg	Na:K
Upper	92	17	12	26	540	13	540	5	nil	2	8.2	7.7	5.4	0.4
Middle	83	14	111	61	950	22	950	15	nil	6	8.0	0.75	5.9	1.8
Lower	80	35	408	73	862	21	962	22	nil	10	8.0	0.2	2.3	5.6
Original soil	145	137	3520	276	4374	23	12100	125	0.21	63	8.4	0.04	1.0	12.0

Soil C : Percentage of original values after leaching

Layer	Ca	Mg	Na	K	Cl	CO$_3$	Total salts	NO$_3$ N	Na$_2$CO$_3$
First	63	12	0.34	9	12	56	4.4	4	3
Second	56	10	3.0	22	22	96	7.8	12	10
Third	55	25	12	26	20	91	7.9	18	16

TABLE XV

Leaching rate in normal and saline soils from Sind (India)

Time in days

Soil type	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Normal soil "A" (o.c.m.)	40	83	130	175	250	320	380	430	510	760	610	690	790	870	930	990	1070	1140	1215	1285	1340
Saline soil "C" (c.c.m.)	230	415	555	680	760	840	915	950	995	1030	1060	1070	1090	1110	1130	1150	1160	1170	1200	1210	1220

TABLE XVI

Average composition of leachings (From Tables XII to XIV)

p. p. m.

Leachings from soils	Ca	Mg	Na	K	Cl	CO3	Total salts	Nitrate N	PO4	Na2 CO3	Ca/Na	Ca:Mg ratio	Na:K ratio	Volume c.c.
A ...	562	142	136	126	394	166	4040	6	0.2	36	4.1	4.0	1.1	450
B ...	852	244	1363	329	2720	90	9710	9	0.06	190	0.6	3.8	4.1	620
C ...	685	665	16305	1144	17885	108	68423	102	0.13	193	0.04	1.0	14.2	1050

TABLE XVII

Composition of soil solutions after capillary rise of leachates through previously leached soil

Figures expressed as p. p. m. on oven dry soil

Soil Layer	Ca	Mg	Na	K	Cl	CO3	Total salts	PO4	Na2 CO3	pH	Ca:Na	Final H20 content	Ca:Mg	Na:K
A Upper	26	6	5	7.9	10	24	219	0.05	5	7.9	5.2	23.2	4.3	0.6
Middle	30	6	10	7.6	10	25	264	0.5	6	7.9	3.0	26.7	5.0	1.3
Lower	120	23	8	17.5	116	21	797	1.0	5	8.2	15.0	27.8	5.1	0.5
Original	101	17.7	25.3	22.6	66	54	616	0.2	11.0	7.6	4.0	..	-5.6	1.1
B Upper	107	18	12	20	16	20	711	nil	5	7.9	8.9	28.1	6.0	0.6
Middle	93	26	29	35	24	28	1120	nil	5	8.3	3.2	29.7	3.5	0.8
Lower	204	75	124	78	2157	13	3436	nil	23	7.6	1.6	33.2	2.7	1.6
Original	187	40	232	45	495	43	1837	0.13	17.0	7.7	0.8	..	4.6	4.2
C Upper	93	12	8	37	41	13	630	nil	9	8.0	11.6	31.3	7.8	0.2
Middle	56	31	177	142	282	32	3270	nil	24	8.4	0.3	31.6	1.8	1.2
Lower	88	298	7923	654	9997	26	31520	nil	51	8.8	0.01	30.4	0.3	12.1
Original	145	137	3520	275	4375	234	12100	0.2	63	8.4	0.04	..	1.0	12.0

TABLE XVIII

Effects of capillary rise of fresh (salt-free) sub-soil water on healthy and saline soils. Distilled water was kept in contact, at bottom, with all the three types of soils—A, B, C.

p. p. m. on oven-dry soil

Soil	Layer	Ca	Mg	Na	K	Cl	CO$_3$	Total salts	PO$_4$	Na$_2$CO$_3$	pH	Ca:Na ratio	ccs. of water risen through pipes	Ca:Mg ratio	Na:K ratio
A	Upper ..	100	19	26	24	65	50	612	0.2	10	7.7	3.8	..	5.2	1.0
	Middle ..	56	10	14	19	21	10	468	0.3	4	8.3	4.0	1160	5.6	0.7
	Lower ..	60	13	25.3	22.6	46	54	600	nil	5	7.8	3.2	..	4.6	0.9
	Original ..	101	17.7	25.3	22.6	46	54	616	0.2	11.0	7.6	4.0	..	5.6	1.1
B	Upper ..	257	53	349	98	950	19	2800	0.2	15	7.6	0.7	..	4.9	3.6
	Middle ..	139	29	253	50	375	55	1760	0.2	10	7.4	0.5	1790	4.8	5.0
	Lower ..	95	17	40	26	25	20	714	0.1	4	8.0	2.4	..	5.6	1.5
	Original ..	187	40	232	45	493	43	1837	0.13	17.0	7.7	0.8	..	4.6	4.2
C	Upper ..	79	121	4266	428	6224	18	15970	nil	8	8.2	0.09	..	0.7	10.0
	Middle ..	97	138	4457	429	5470	39	10980	nil	51	9.2	0.02	1920	0.7	13.9
	Lower ..	52	17	743	316	155	43	7985	nil	125	9.0	0.07	..	3.0	2.4
	Original ..	143	137	3520	275	4375	23	12100	0.2	63	8.4	0.04	..	1.0	12.0

TABLE XIX

*Effect of capillary rise of †saline sub-soil water on healthy and partially saline soils

Soil Layer		Ca	Mg	Na	K	Cl	CO_3	Total Salts.	PO_4	Na_2CO_3	pH	Ca:Na ratio	ccs. of water rising in pipe	Ca:Mg ratio	Na:k ratio
A	1st (surface) ..	165	23	42	31	270	12	1258	0.05	nil	8.4	4.0	..	7.0	1.3
	2nd (Middle) ..	763	205	467	92	2543	8	6142	nil	1.4	7.6	1.6	1590	3.7	5.0
	3rd (Middle) ..	320	117	1518	87	3607	11	7689	nil	3.3	8.1	0.2	..	2.8	17.4
	4th (lower) ..	156	110	1438	32	3032	7	6992	nil	nil	8.0	0.1	..	1.4	45.0
	Original ..	101	17.7	26.3	22.6	66	53	616	0.24	11.0	7.6	4.0	..	5.6	1.1
B	1st (surface) ..	249	62	316	72	984	8	3118	nil	5.1	7.6	0.8	..	4.0	4.4
	2nd (Middle) ..	413	90	394	121	1742	8	4056	nil	10.3	7.6	1.0	1460	4.6	3.3
	3rd (Middle) ..	370	136	1334	125	3291	9	6696	nil	17.2	8.4	0.3	..	2.7	3.3
	4th (lower) ..	207	137	2086	62	4007	9	8947	nil	nil	7.7	0.1	..	1.5	33.6
	Original ..	187	40	231	45.5	493	234	1837	0.13	17.0	7.7	1.8	..	4.6	4.2

*Soil columns are broken into 4 layers to observe the effect on successive layers.

†Containing Ca (625), Mg (450), Na (8700), Cl (9100)—Parts per million.

Preparation:—NaCl 1.5%, Na_2SO_4 0.5%, $MgSO_4$ 0.4% in saturated solution of $CaSO_4$.

TABLE XX

* Sind soils were packed in glass tubes of 1" diameter

Capillary rise in normal and saline soils under fresh and salt water conditions at bottom (c.ms.)

Type of soil Type of water used	Time in days										
	1	2	3	4	5	6	7	8	9	10	11
Normal soil with fresh water	22	41	51	59	67	73	78	83	87	91	94
Saline soil with fresh water	36	60	70	78	85	90	96	101	107	111	116
Normal soil with salt water	44	67	82	93	102	109	118	126	131	136	..
Saline soil with salt water	31	58	72	80	88	94	100	105	112	117	120

* Composition of salt water was the same as that of one used in drain pipes. i.e., solution of NaCl, Na_2SO_4 and $MgSO_4$ in saturated solution of $CaSO_4$.

(See Fig. 3)

TABLE XXI

Rise of fresh water in drain pipe lysimeter with different types of Sind soils

Rise expressed in cubic centimeters

Type of soil	Time in days.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A—Normal	370	660	820	920	950	1000	1020	1030	1050	1070	1110	1150	1180	1210	1240
B—Medium Saline	200	430	620	770	920	1060	1160	1270	1380	1460	1540	1650	1680	1760	178
C—Saline	290	490	670	850	1020	1130	1250	1370	1460	1560	1660	1740	1820	1860	192

(See Fig. 4)

TABLE XXII

Soil solution and plant (wheat) performances in pots

Soil	Results of analyses (by soil solution methods)										Yield of wheat grain and total dry matter per pot of 3 plants (av. of 4 pots)	
	Total soluble matter	Parts per million on dry soil								pH	Grain grams	Total dry wt. grams
		Ca	Mg	Na	K	Ca:Na ratio	Ca:Mg ratio	NO$_3$	PO$_4$			
(i) Soil of high fertility	1200	150	23	27*	45	5.5	6.5	11	0.8	7.4	182	528
(ii) Soil of low fertility	400	80	23	18	20	4.5	3.5	3	0.6	7.8	55	136
(iii) Soil (i) after receiving a leaching with 24 inches of water	250	40	16	13.3	18	3.0	2.5	2	0.4	8.2	64	147
(iv) Leached soil (iii) treated with sulphate of Am=30 lbs. N.p.a. and superphosphate =50 lbs. P$_2$O$_5$ p.a.	600	101	25	20	20	5.0	4.0	6	0.8	7.4	96	212
(v) Leached soil (iii) treated with its * leachates as irrigation water	1150	140	25.5	25.5	42	5.5	5.5	9	0.8	7.4	179	465

* Analyses of leachate is given elsewhere. Pots (i-iv) were irrigated with engine distilled water (containing 20 p.p.m. solids).

Note.—Qualitatively it was observed that the quality of grain was superior in case of (i) and (v) treatments.

Capillary Rise of Moisture in Drain Pipes, *vide Table IX*

O   Soil (without salt) and pure water (Devon soil) pipe No. 6

△   Soil (with 10% NACL)   ,,   ,,   ,,   ,,   ,,   ,,   7

✕   Soil and 15% NACL Solution   ,,   ,,   ,,   ,,   ,,   8

THREE FEET SOIL COLUMN.

Fig. 1
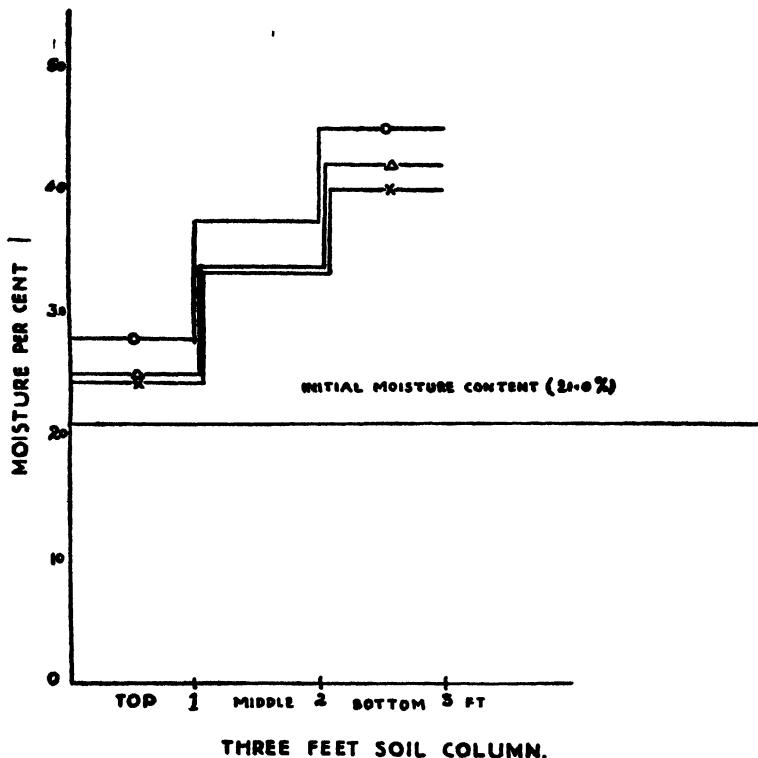
Leaching Rate in Normal and Saline Soils from Sind (India), *vide Table XV*
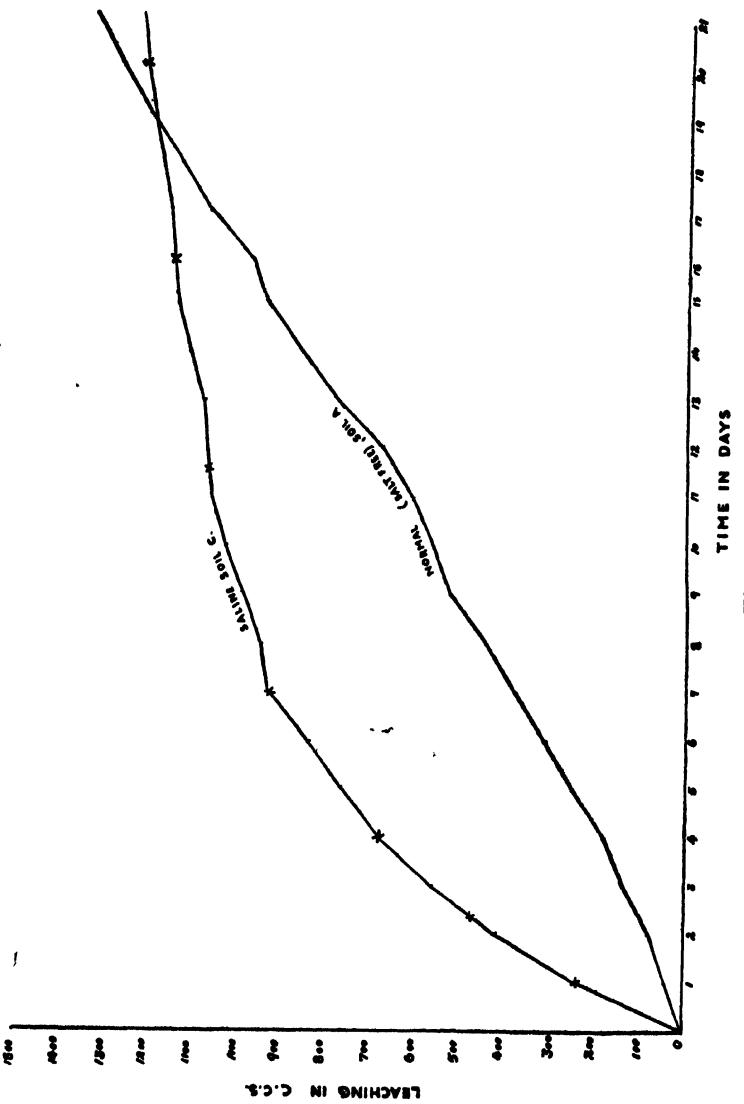
Fig. 2

(Glass Tubes)
expt

Capillary Rise in Normal and Saline Soils under Fresh Water and Salt Water Conditions (Sind Soils)

vide Table XX.

NORMAL SOIL (WITH SALT WATER)

(b) SALINE SOIL (WITH SALT WATER)

(b) SALINE SOIL (WITH FRESH WATER)

NORMAL SOIL (WITH FRESH WATER)

RISE IN Cms.
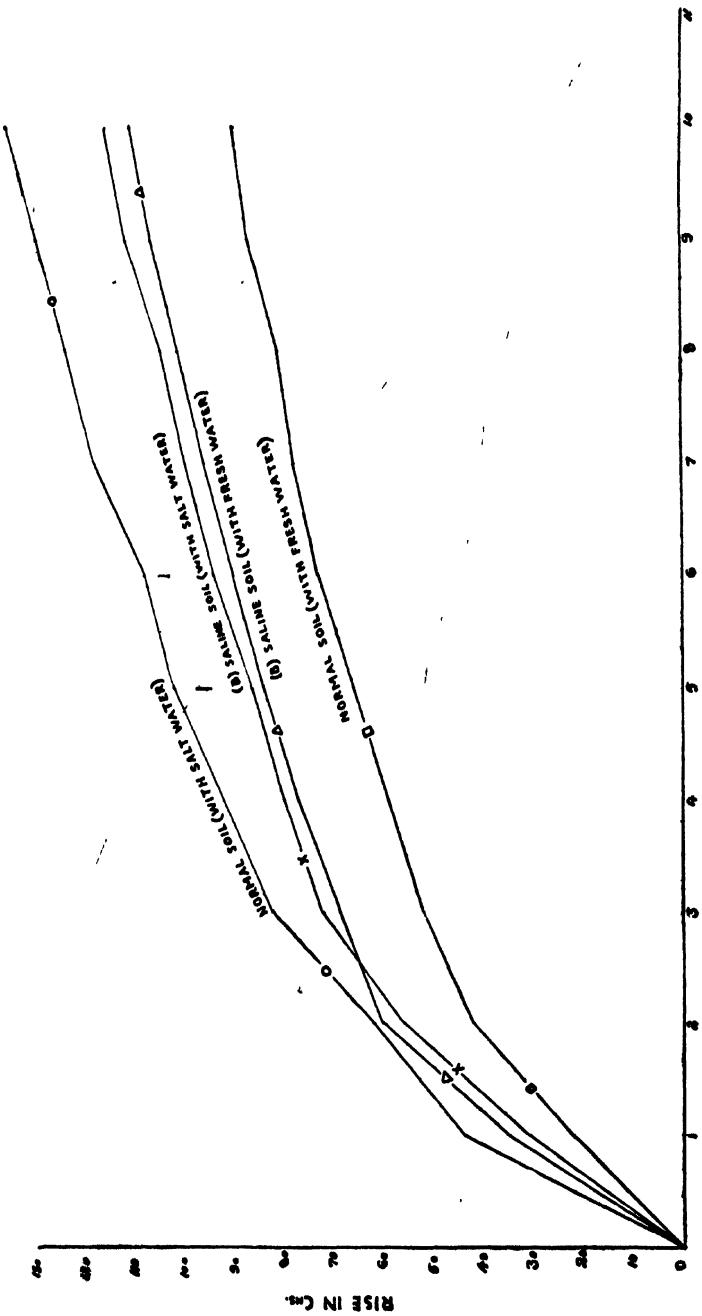
Fig. 3

Volume of Fresh Water absorbed by different
Sind Soils in the Drain Pipes, *vide Table XXI*
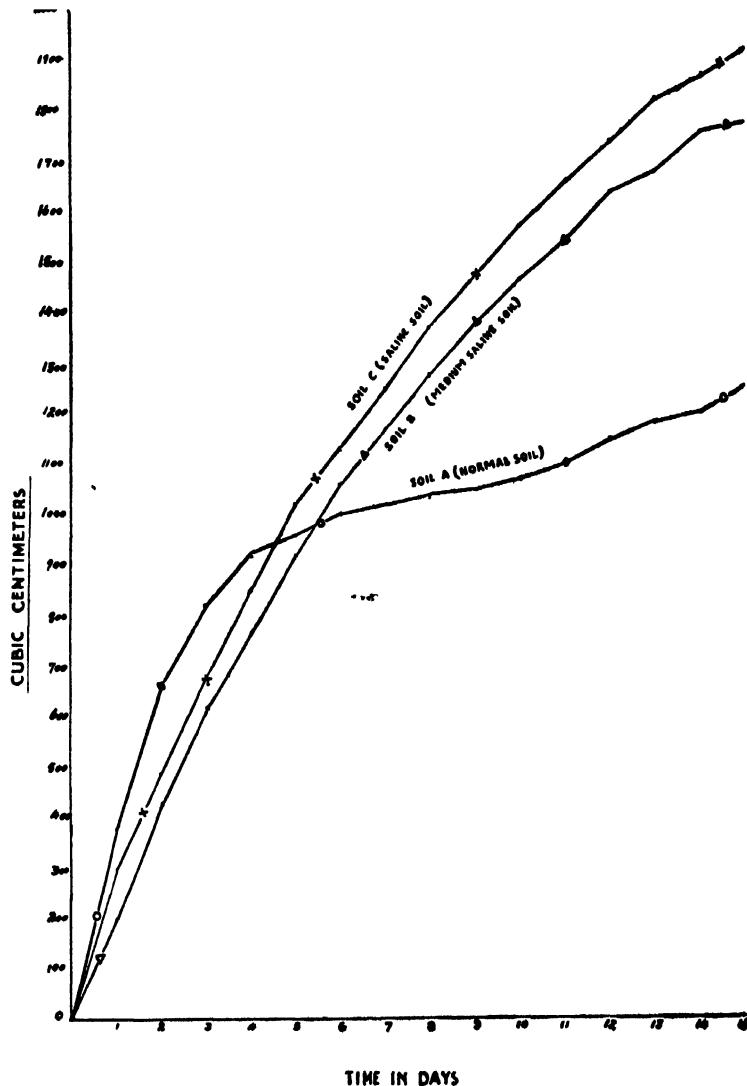
Fig. 4

Different sizes of Laboratory Lysimeters, *vide Tables VI & VI a*
(No. 3 is suitable size)

1. Small bottle size
2. Medium size
3. Big size
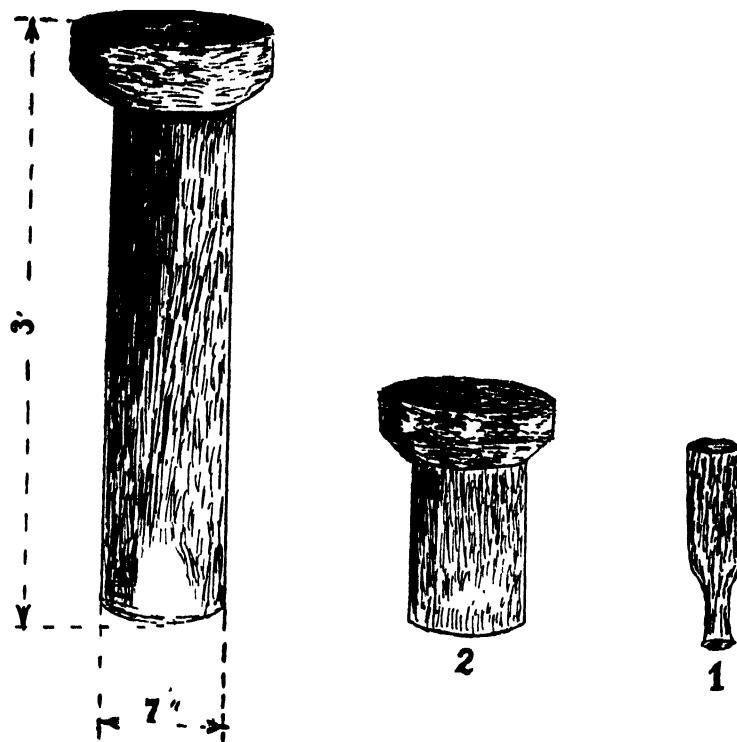
Plate I

Drain Pipe Lysimeters (1 to 4 different views)

No. 4 shows a complete "Rack" of three feet size Lysimeters in series of six (in working positions)

1

2

3

4
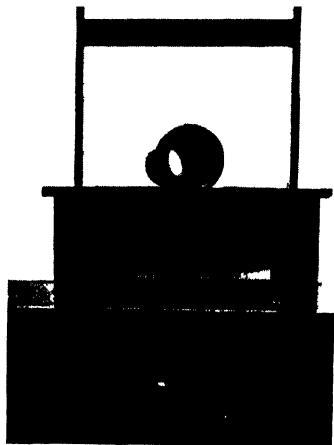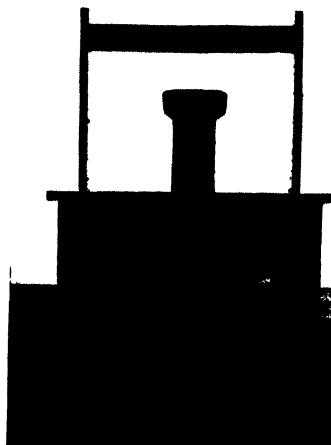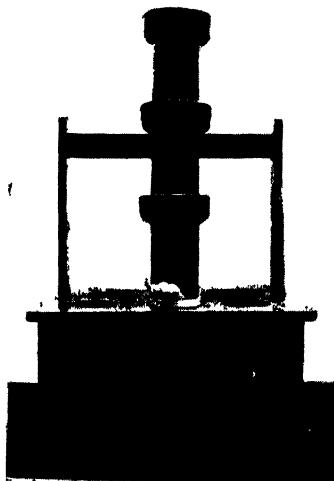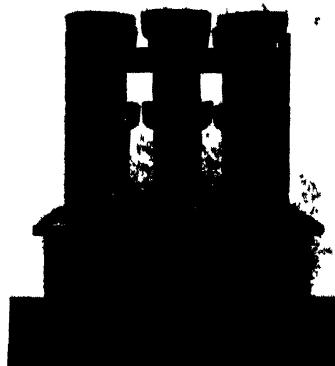
Plate II

Enlarged Photo of Drain-Pipe Lysimeters,
vide No. 4 of plate II
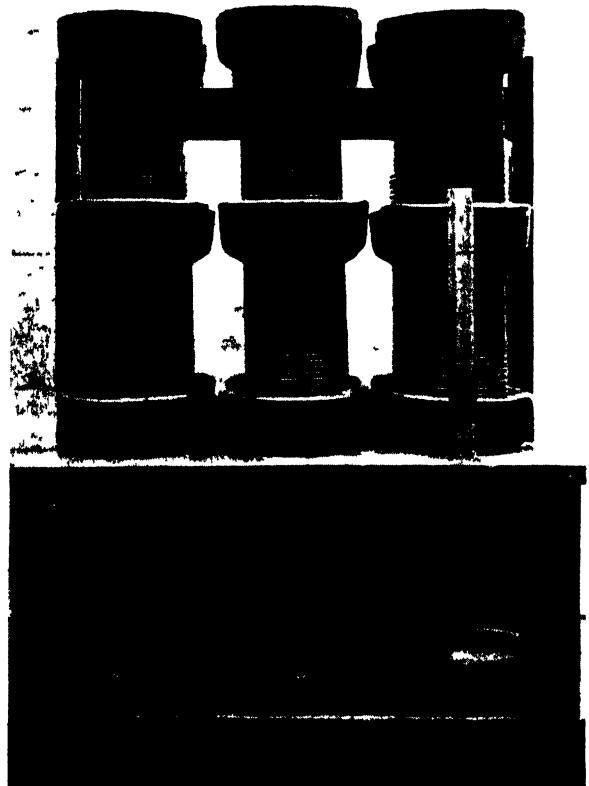
Plate III

BROMINATION OF ORTHO-NITRO-TOLUENE, AND THE STERIC EFFECT OF THE BROMINE ATOM ON THE RELATIVE YIELDS OF THE 4 AND 6 BROMO-DERIVATIVES

By

D. R. MEHTA AND P. RAMASWAMI AYYAR

INTRODUCTION

A REVIEW of the literature (J. Chem. Soc., 1929, 1243) on bromo-nitro-toluenes showed that all the bromo-nitro-toluenes have only been made by very indirect methods and that none of them has been prepared in the pure condition by the direct process of bromination of the corresponding nitro-toluene. The direct bromination of ortho-nitro-toluene results in the formation of dibrom-anthranilic acid and tribrom-aniline (Wachendorff, Ann, 1877, *185*, 259, Greiff, Ber., 1880, *13*, 288, Yabroff, J. Amer. Chem. Soc., 1932, *54*, 3011). The above complications in the direct bromination of ortho-nitro-toluene arise, however, only in the absence of a catalyst and when a high temperature (170°C) has necessarily to be used. In fact, Wilhelm Gluud (Ber. 1915, *48*, 432) showed that nuclear bromination of ortho-nitro toluene proceeds quite smoothly with iron powder as a catalyst,and he found that 4-bromo-2-nitro-toluene was the main product. The re-action product, however, was found very resistant to oxidation by potassium permanganate yielding only small quantities of 4-bromo-2-nitro-benzoic acid and a substance (m.p. 178°C) which was believed to be 6-bromo-2-nitro-benzoic acid.

Comparative steric effect of the bromine-atom :—

The non-formation of 6-bromo-2-nitro-toluene in a larger proportion, in the above reaction, seemed of considerable interest because Gindraux (Helv, Chim, Acta, 1929, *12*, 921) has chlorinated ortho-nitro-toluene with an iron catalyst and obtained a 66 per cent. yield of 6-chloro-2-nitro-toluene and 34 per cent. only of 4-chloro-2-nitro-toluene. It looked as though the larger atomic volume of the bromine atom hindered the intro-duction of the same into the 6-position because of consequent crowding together of three groups in three adjacent positions (6 : 1 : 2) of the benzene nucleus in the molecule of ortho-nitro-toluene.

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It was, therefore, considered necessary to re-examine this question of the nuclear bromination of ortho-nitro-toluene with and without catalysts, and to evolve a more satisfactory and a quantitative method of estimating the relative amounts of the isomeric bromo-nitro-toluenes formed in the various reactions.

Outline of the present bromination of ortho-nitro-toluene :—

The bromination of ortho-nitro-toluene was first tried with pyridine alone as catalyst, and then with addition of concentrated sulphuric acid. Ferric sulphate in sulphuric acid was next tried as a catalyst   In these cases we could not isoláte any bromo-nitro-toluene but only dibromanthranilic acid (Yabroff, J. Amer. Chem. Soc., 1932, *54*, 3011) and tribrom-aniline.

Hence, the following catalysts were employed successively : iron, iron and iodine, antimony trichloride, antimony tribromide and antimony pentachloride, to study the nature and extent of nuclear bromination occurring in ortho-nitro-toluene.

Nature and proportions of the reaction products :—

The reaction product in each case was fractionally distilled under reduced pressure and the first portions of unattacked ortho-nitro-toluene were set aside.   The residual product after being distilled consists of the mixed 4- and 6-bromo-nitro-toluenes.   The formation of other mono-bromo-substituted nitro-toluenes was not, ordinarily, to be expected. The formation of any dibromo-substituted compound also was not likely in view of the experiments carried out by Wilhelm Gluud and Gindraux. Still it was necessary to prove the same by some reliable chemical method.

On the analogy of the mild and nearly quantitative oxidation of acet-o-toluidide and its substituted halogen derivatives to the corresponding acetamino-benzoic acids by aqueous potassium permanganate in presence of magnesium sulphate, we reduced the mixed bromo-nitro-toluenes to the mixed amino-derivatives and the latter were then converted into the corresponding mixed acetamino-bromo-toluenes. These were then oxidised with neutral aqueous permanganate to the corresponding known acetamino-bromo-benzoic acids (Ann, 1912, *388*, 29; *ibid.*, 1875, *172*, 223). The mixed 4- and 6-bromo-2-acetamino-benzoic acids lent themselves to a fairly easy and quantitative separation from each other in a pure state, and no other similar acetamino-bromo-acid could be detected even in small quantities in the above oxidation product.   It was thus proved by chemical evidence that no bromo-nitro-toluene was formed (except perhaps in undetectable traces) in the catalytic bromination of ortho-nitro-toluene other than the 4- and 6-bromo-compounds.   The relative proportions of the bromo-nitro-toluenes, determined by the above chemical method, was about 56 per cent. of the 4-bromo, and 44 per cent. of the 6-bromo-2-nitro-toluenes.

Solidification-points-curve of a mixture of 4- and 6-bromo-nitro-toluenes :—

In addition to the above chemical method, it was thought advisable to confirm the above results independently by an easily applicable direct

method by means of which the proportions of the two isomerides can readily be determined.

As no suitable data were available in the literature, the solidification points of a mixture of these two isomerides were determined, and these were plotted against their percentage composition in the form of a graph. In using the above graph for analytical purposes, the sense of change of solidification point of a reaction mixture with further addition of one of the pure isomers, definitely settled the position of the point on the graph and hence its percentage composition.

Pure 6-bromo-2-nitro, (Ann, 1912, *388*, 29 ; *ibid.*, 1875, *172*, 223) and 4-bromo-2-nitro-toluenes (Ann, *155*, 14) were prepared specially for this work by the known indirect methods available in the literature starting from 2 : 6-dinitro-toluene and 2 : 4 dinitro-toluene respectively, introducing necessary improvements and modifications in the existing mode of reduction of the dinitro-compounds (see experimental part) and diazotisation of the resulting nitro-amino-toluenes.

Use of the graph for analytical purposes :—

From the graph the percentages of 4-and 6-bromo-nitro-toluenes in the mixtures obtained in the present bromination, could be read, once their solidification points were determined. The following table gives a summary of the results obtained with various catalysts :—

No.	Catalyst	Amount of product taken	Amount of 4-bromo-2-nitro-toluene added	Solidification points	Percentage of 4-bromo-2-nitro-toluene
I	Antimony pentachloride	3.2860	*nil*	13.3	56
	do. ..	3.2860	0.3110	16.8	
II	Iron powder ..	3.0859	*nil*	12.3	55.25
	do. ..	3.0859	0.2897	15.8	
III	Iron+iodine ..	2.2628	*nil*	16.7	59
	do. ..	2.2628	0.2134	19.1	
IV	Antimony trichloride ..	....	....	4.9	....

The product IV in the above table seemed to be admixed with unchanged o-nitro-toluene and hence was not taken into consideration.

It was found that iron *plus* iodine is the most active catalyst, the reaction starting and completing itself entirely in the cold. In other cases the reaction mixture had to be warmed on a water-bath or heated under reflux to a high temperature in an oil bath, at one or the other stage in the reaction.

As will be seen the relative proportions of the bromo-nitro-toluenes determined by the chemical and the physical methods agree well.

Conclusion :—

These results show in a remarkably interesting manner that bromine in comparison with chlorine forms, probably by reason of its larger atomic volume (or parachor), much less 6-substituted derivative than the 4-substituted compound. The steric effect, judged by the yields actually observed in this investigation is in the ratio of Br : Cl, 66 : 43 or roughly 3 : 2.

Experimental

Bromination of ortho-nitro-toluene with the following catalysts :—

(a) *Pyridine :—*

Pure pyridine at boiling water-bath temperature with and without carbon tetrachloride as a solvent, gave only unchanged o-nitro-toluene. Pure pyridine in aqueous solution in the cold, and with addition of concentrated sulphuric acid also gave mostly the unchanged o-nitro-toluene.

(b) *Pyridine at* 110°—30°C *:—*

Ortho-nitro-toluene (10 gms.) and pyridine (6 gms.) were placed in a flask fitted with a reflux condenser and heated in an oil-bath with gradual addition of bromine (5 c.c.). The temperature was maintained between 110° and 130°C. When all the bromine was added up (it took about an hour and a half) the product was allowed to cool. It was then poured on to four or five times the quantity of water and extracted with ether. The ether extract was washed with water and then with dilute sodium carbonate solution to remove the acidic portion (A). It was once more washed with water and ether removed. The solid residue was once washed with a little chloroform and crystallised from alcohol. It gave beautiful needles m.p. 119°C (yield : 0.6 gm.). The sodium carbonate solution (A) was acidified, saturated with common salt and extracted with ether. The ether was washed with a little water and ether removed. The solid residue, when crystallised from dilute alcohol, gave microscopic needles m.p. 227°—8° (yield : 0.4 gm.). Equivalent : 292.3 ; that of dibromanthranilic acid, $C_7H_3.O_2N$ Br_2 being 295). These substances were identified as tribromaniline (m.p. 119°C)and dibromanthranilic acid (m.p. 227°—8°) by mixed melting points as well as by analysis.

*Analysis :—*Substance m.p. 119° (Found : Br, 72·03 ; N, 4.34, C_6H_4N Br_3 requires, Br, 72.7, N, 4.24 per cent.) Substance m.p. 227°—8° $_2$ (Found : N, 4.78, $C_7H_5O_2N$ Br_2 requires, N, 4.74 per cent.)

(c) *Ferric sulphate (anhydrous) and concentrated sulphuric acid :—*

This experiment gave a small quantity of a substance m.p. 225°—26° (yield : 0.5 gm. from 10 gms. of o-nitro-toluene). This substance was found to be identical with dibromanthranilic acid obtained in (b).

(d) *Iron powder :—*   •

Bromine (12.5 c.c.) was added drop by drop to a mixture of o-nitro-toluene (25 gms.) and iron powder (5 gms.) in a flask fitted with a reflux

condenser. There was no perceptible reaction in the cold. On warming the flask for a few minutes on the water-bath, a vigorous reaction took place, which completed itself in the cold in about an hour. The product was treated with water and extracted with ether. The ether extract was washed with water, dried and the ether removed. (In a preliminary experiment the ether extract was washed with Na_2Co_3 solution but on acidifying the Na_2Co_3 solution and extracting with ether no acidic portion could be obtained). The residual liquid (36 gms.) gave on distillation two fractions : (i) b.p. 140-50°/35 m.m. and (ii) b.p. 150-60°/35 m.m. The b.p. of o-nitro-toluene at 35 m.m. was found to be 117°-19°C. Yield of the brominated product was nearly quantitative.

(e)   Iron + Iodine :—

A mixture of o-nitro-toluene (25 gms.), iron powder (2 gms.) and iodine (0.2 gms.) was taken in a flask and bromine (15 c.c.) added drop by drop. The reaction started in the cold without the application of external heat, and had to be regulated by decreasing the rate at which bromine was added. At the end of the reaction, the flask was warmed up on the water-bath to ensure the completion of the reaction. The product when distilled gave 23 gms. of a liquid b.p., 147°-8°/35 m.m. 6 gms. of a liquid b.p. 148°-50°/35 m.m. and 4 gms. of a brown oil as a residue. Yield of the brominated product : 85 per cent.

(f)   Antimony metal, antimony trichloride :—

With antimony metal as a catalyst most of the o-nitro-toluene was recovered unchanged. With antimony trichloride as a catalyst, only partial bromination took place yielding : (i) a liquid b.p. 125°-35°C/35 m.m. and (ii) a small quantity of a liquid b.p. 135°-50°C. The reaction was carried out using carbon tetrachloride as a solvent.

(g)   Antimony pentachloride :—

After a preliminary experiment with small quantities using antimony pentachloride as a catalyst, the following experiment was carried out with larger quantities :—

137 gms. ortho-nitro-toluene.

80 gms. antimony pentachloride (added in small lots when the reaction with each lot became slow).

70 c.c. Bromine.

The experiment was carried out in a three-necked flask, fitted with a mechanical stirrer. Bromine was added up during five hours, at the end of which the flask was heated to 80°C on a water-bath for some time. The product after cooling was washed with hydrochloric acid (1 : 1), then with water, then with 2N sodium hydroxide solution, and again with water. It gave 190 gms. of a liquid which after mixing with 30 gms. of a similar product obtained from a preliminary experiment, was fractionally distilled. On repeated fractionation, it gave a liquid

(35 gms.) boiling below and up to 145°/35 m.m. which was set aside and a liquid b.p. 147°-52°/35 m.m. (165 gms.). This latter liquid, on further fractionation, gave 155 gms. of a liquid distilling at 150°-152°/35m.m. This liquid was used for the solidification points, and the reduction and oxidation experiments described later. (Found : Volumetric, Br,36.6, $C_7H_6O_2N$ Br requires Br, 37.0 per cent.).

Proof that antimony pentachloride does not halogenate the ortho-nitro-toluene by itself :—

In order to prove this, a blank experiment was carried out, with antimony pentachloride (2 gms.) and o-nitro-toluene (5 gms.). o-nitro-toluene was recovered unchanged.

Proof that substitution by bromine is nuclear :—

The mixture of isomers (b.p. 150°-2°) (2 gms.) obtained above was boiled with alcoholic potash (20 per cent.) for four hours under reflux. Alcohol was then distilled off and the residue extracted with ether. The ether extract was washed, dried and the ether removed. The resulting product contained nitrogen and bromine.

Preparation of 4-amino-2-nitro-toluene :—

2 : 4-dinitro-toluene (50 gms.) was added to a mixture of liquor ammonia (50 c.c.), benzene (350 c.c.) and alcohol (350 c.c.) so as to keep the dinitro-toluene in solution. The mixture was cooled in ice, and a current of hydrogen sulphide passed through it for about 3—4 hours till there was no further absorption. The solvent was then distilled off, and the residue repeatedly extracted with dilute hydrochloric acid and filtered. The acid filtrate was made strongly alkaline and filtered. The residue of 4-amino-2-nitro-toluene was crystallised from a large quantity of water and gave golden yellow leaflets (m.p. 79-80°C). Yield : 35 gms.

If the reduction is carried out in alcoholic solution as previous workers (Ann, *155*, 14) have done, much of the dinitro-toluene remains undissolved and the yield of the amino-compound is very low. Benzene was therefore used to get all the dinitro-toluene in solution. This method gives practically a quantitative yield.

Preparation of 4-bromo-2-nitro-toluene :—

A mixture of 4-amino-2-nitro-toluene (21.7 gms.) obtained above, concentrated hydrochloric acid (33 gms.) and water (375 c.c.) was cooled to 0°C, in a flask fitted with a mechanical stirrer, and diazotised with 2N-sodium nitrite solution (75 c.c.). After allowing it to stand in the cold for some time, it was decomposed with a solution prepared by boiling a mixture of copper sulphate (18.6 gms.), potassium bromide (72 gms.), concentrated sulphuric acid (16.5 gms.), copper powder (22.5 gms.) and water (420 c.c.).

The well-mixed solution was allowed to stand for about 3 hours, then warmed on a water-bath for half an hour and the liquid after cooling,

extracted with ether. The ether extract was dried and the ether removed (crude product, yield : 15 gms.). The product was then steam-distilled in dilute alkali suspension, and the distillate extracted with ether. The ether extract was dried and the ether distilled off. The residue on being crystallised from alcohol gave stout needles (m.p. 44°C).

Preparation of 6-amino-2-nitro-toluene :—

The same method as in the preparation of 4-amino-2-nitro-toluene was employed, but no benzene was used in this case. A mixture of 2 : 6-dinitro-toluene (30 gms.), 90 per cent. alcohol (90 c.c.) and concen. ammonia (75 c.c.) was placed in a flask and a current of hydrogen sulphide passed as before, till no more was absorbed. Proceeding as in the preparation of 4-amino-2-nitro-toluene, a residue of 6-amino-2-nitro-toluene was obtained which could be crystallised from dil. alcohol (m.p. 91°C). Yield : 16 gms.

Preparation of 6-bromo-2-nitro-toluene :—

The same method was employed as in the preparation of 4-bromo-2-nitro-toluene. From 14.5 gms. of the nitro-toluidine obtained above, 15.5 gms. of the crude 6-bromo-2-nitro-toluene was obtained, which after steam-distillation in dil. alkali suspension, and crystallisation from ether gave a product m.p. 39°C.

Solidification points of the mixed 4-and 6-bromo-nitro-toluenes :—

Weighed quantities of the two isomeric compounds were introduced into a specially designed jacketed test-tube, making arrangements for the inner tube containing the mixture to carry a nickel-stirrer and a standardised thermometer reading to a tenth of a degree. The mixture is first melted, well mixed, and then allowed to cool gradually to determine the solidification point roughly. The tube is then warmed up again till the solid melts, and again cooled, this time taking care to begin stirring the mixture a few degrees above the solidification point. In this process, the liquid gets cooled below the solidification point, and then suddenly the thermometer thread shoots up and the temperature remains constant at the real solidification point for some time. The experiment is repeated till closely agreeing solidification points are obtained with each mixture.

The table (I) showing the solidification points of various mixtures and the quantities in each case is given below. A graph drawn to illustrate the relationship between the solidification points and percentage composition is given on page 107.

TABLE I

Mixture No.	Amount of 0-bromo-2-nitro-toluene in gms.	Amount of 4-bromo-2-nitro-toluene in gms.	Total weight of the mixture in gms.	Percentage of 4-bromo-2-nitro-toluene in the mixture	Solidification points
	Nil	2. 923	....	100	41.6
I	0.3464	2.4110	2.7574	87.47	34·9
II ..	0.6976	2.1748	2.8724	75.71	26.2
III ..	0.8480	1.6628	2.7108	66.2	22.25
IV ..	1.1140	1.6830	2.7970	60.1	17.8
V ..	1.5336	2.0792	3.6128	57.5	14.3
VI ..	1.5529	1.8736	3.4265	54.6	11.8
VII ..	1.5789	1.7172	3.2961	52.0	9.2
VIII ..	1.6591	1.6575	3.3166	49.9	7.9
IX ..	1.6184	1.3082	2.9266	44.7	6.0
X ..	1.6446	1.203	2.8476	42.2	7.7
XI ..	1.7677	1.2899	3.0576	42.1	7.8
XII ..	1.5404	1.0286	2.5690	40.0	9.2
XIII ..	1.656	1.012	2.668	37.8	11.2
XIV ..	1.9293	1.0077	2.9370	34.3	16.0
XV ..	2.7179	0.9285	3.6464	25.4	22.0
XVI ..	2.1761	0.3266	2.5027	13.4	29.2
	2.9803	*nil*	....	0	37.1
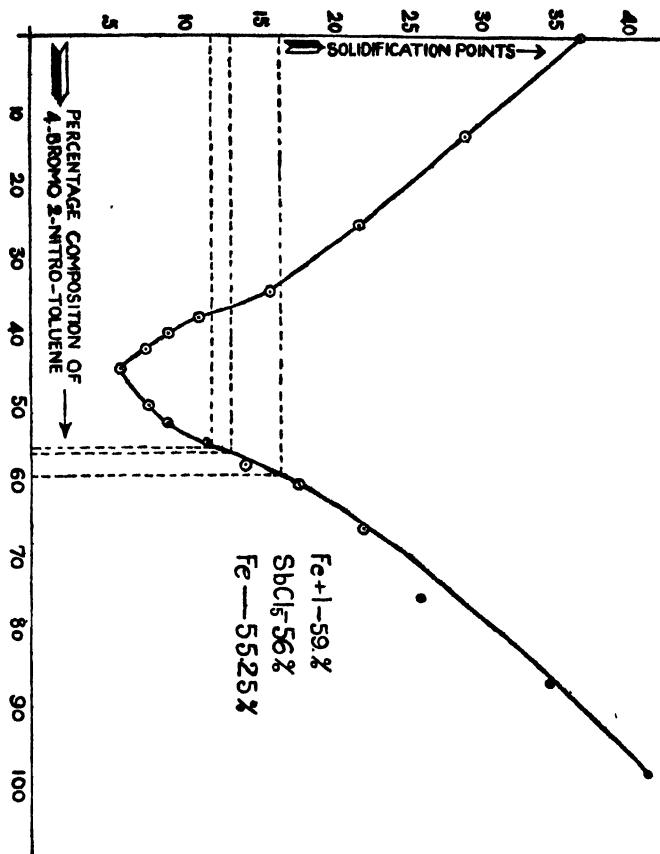
Solidification points of the reaction products and conclusions re : their percentage compositions :—

' The solidification points of products obtained in cases where iron powder, iron and iodine, antimony trichloride, and antimony pentachloride were used as catalysts were found out and the percentage composition of the product in each case was determined by the help of the graph. The results are given on page 106.

Reduction of the reaction product (catalyst, antimony pentachloride) to the mixed amino-compounds :—

The bromo-nitro-toluene mixture (5 gms.) and iron-powder (6 gms. excess) were taken in a flask fitted with a reflux condenser, and hydrochloric acid (1 : 1) was added as required, the flask being heated with a small flame. When all the heavy layer at the bottom had disappeared, the liquid was allowed to cool, and then shaken with ether to remove any unchanged bromo-nitro-toluene. The acid solution was then made strongly alkaline with 2N sodium hydroxide solution and extracted

7 (a)

with ether. The ether extract was dried and the ether removed. A low melting liquid was left behind. Yield : 4.2 gms. (quantitative).

Acetylation of the mixed bromo-amino-compounds and attempts at isolation of pure acetyl derivatives :—

Acetic anydride (6 gms. excess) was added to the mixed bromo-amino compounds (4.2 gms.) in a flask. The flask was warmed up and on cooling the contents solidified. The flask was heated under reflux on an oil-bath (140-50°) for about an hour to complete the reaction. The reaction mixture was then poured into water and after vigorous stirring with addition of some sodium carbonate, it was ether extracted. The ether was removed after drying the extract. A thick liquid resulted (Yield : 5.06 gms.). This was reserved for the quantitative oxidation experiment which is described later. The acetylation experiment was repeated and the reaction mixture was poured on to water as before. It was constantly stirred and allowed to stand for four days, when it became a semi-solid. An attempt to separate the constituents of thi-. semi-solid resulted in the isolation of a small quantity of a pure sub. stance m.p.163-64°C and various mixtures melting from 128°-135°Ce The compound, m.p. 163-164°C appears to be either pure 4-bromo- or 6-bromo-2-acetamino-toluene, since the m.ps. of both these compounds are close together (Ann, *398*, 359 ; Soc. *85*, 1627; Ann *388*, 29; Ann *172*, 223; Soc. *105*, 514). This method of separation was however abandoned.

Oxidation of the mixed acetamino-compounds and quantitative separation of 4-bromo- and 6-bromo-2-acetamino benzoic acids :—

The bromo-acetamino-toluene (5 gms.), potassium permanganats (10 gms.), magnesium sulphate crystals (10 gms.) and water (625 c.c.) were heated in a three-necked flask fitted with a mechanical stirrer. The temperature was maintained between 85-95°C for about four hours. The heating was then stopped and after cooling, sulphur dioxide was passed through the solution, till it was clear. The liquid was then saturated with sodium chloride, and extracted with ether several times. The acidic solution after ether extraction, contained a solid in suspension, which was filtered, dissolved in dilute sodium carbonate, filtered again and the sodium carbonate solution acidified. A precipitate separated out, which when crystallised from alcohol, melted at 222-23°C (A), (Yield : 1.2 gms.). ·The ether extract was washed with dilute sodium carbonate solution and then with water to remove the ether soluble acids formed. From the residual ethereal solution, ether was removed, and unoxidised substance recovered (0.2 gms.). The sodium carbonate solution used to wash the ethereal solution was acidified, when a thick precipitate separated out, which was filtered (2.5 gms.). This precipitate when crystallised from dilute alcohol gave crystals which melted at 217°C (B). The filtrate obtained after filtering the precipitate B, gave on cooling star-shaped crystals m.p. 220°-21°C (A). This solution was saturated with common salt and extracted with ether some fifteen times and the ethereal solution distilled off when a small quantity of a substance m.p. 222°C was left behind. The dilute alcoholic mother liquor obtained from the crystallisation of acid m.p. 217°C (B) also gave a small quantity

of an acid identical with that obtained of m.p. 222-23°C (A). The mixed melting point of the acid (A) with the acid (B) was found to be 200-3°C, so that acids (A) and (B) were different individuals. Their almost quantitative separation from the mixture depended upon the relative insolubility in ether of one of them (A), as also the greater solubility of the same in dilute alcohol, combined with the sparing solubility of the other (B) in dilute alcohol and its ready solubility in ether. 6 bromo- and 4-bromo-2-acetamino-benzoic acids are known and melt at 224°C and 217°C respectively as found by previous workers (Soc. *105*, 514).

Hence the acid (A) was 6-bromo-2-acetamino benzoic acid (total yield : 1.5 gms.) and the acid (B) the 4-bromo-2-acetamino-benzoic acid (total yield : 2.0 gms.). Taking the relative yields of the two acids as a guide to the relative proportions of the isomeric bromo-nitro-toluenes present in the original reaction product, the ratio of ortho to para-substitution works to 42 : 56. This proportion agrees remarkably well with the proportions of the two isomerides obtained by the method of solidification-points-determination (43 : 57).

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STUDIES ON ISOCYANATES: THE REAC-TION BETWEEN PHENYLISOCYANATE AND SODIUM PHENYL-ACETYLIDE

By

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D. E. WORRAL (J. Am. Chem. Soc., *1917*, 697 ; *1937*, 933, 1486) has reported that isothiocyanates react with sodium phenyll acetylide to afford amides or anilides of thiopropiolic acid :

$$C_6H_5NCS + NaC : CC_6H_5 = C_6H_5NHCSC : CC_6H_5$$
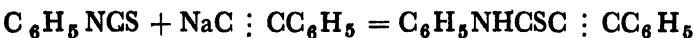
In this particular case the adduct is unstable to heat and to acids and if warmed in alkaline solution, polymerises to the alkali-soluble product:

$$C_6H_5C : CHCSNHC_6H_5$$
$$\overset{|}{S}$$

$$C_6H_5N: C.C : CC_6H_5$$
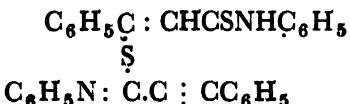
Smith and Hoehn (J. Am. Chem. Soc., *1939*, 2619), on investigating the reaction between diphenylketene and phenyl-acetylene, have isolated 3 : 4-diphenyl-α-naphthol as the reaction product. No cyclobutanone derivative appeared to have been formed. These authors gave no explanation for the reaction, which may be formulated in the following manner :
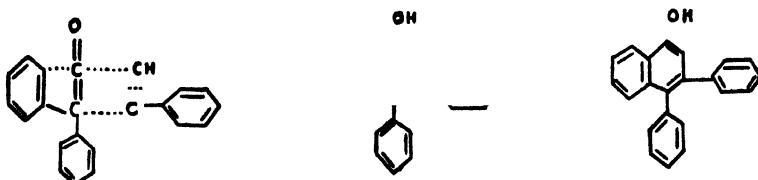
In view of the fact that isocyanates and isothiocyanates have been found to react analogous to the ketenes (Staudinger, "Die Ketene," further, C. Naegeli and A. Tyabji, Helv. Chim. Acta, 1934, *17*, 931, 1935, *18*, 142) it was of interest to investigate the type of reaction between phenylisocyanate and phenylacetylene to determine whether a straight chain anilide is formed or a ring compound corresponding to the α-naphthol derivative formulated above.

Phenylisocyanate and phenylacetylene did not react together, but when sodium acetylide was used, three different condensation products

could be isolated, two of which are coloured and consist of the components in the ratio of two molecules of phenylisocyanate to one molecule of phenylacetylene and of one molecule phenylacetylene to three molecules of phenylisocyanate in the third product. One of the compounds might have been the phenylcarbamate of 2-phenyl-4-oxyquinoline, the ring compound corresponding to Smith and Hoehn' α-naphthol derivative : but the quinolinol, a white compound, was found to be unreactive towards phenylisocyanate.
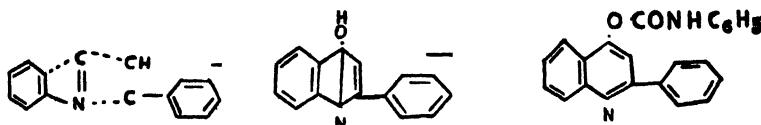
Lack of chemicals has unfortunately prevented a more detailed investigation of the three new compounds with a view to establish their chemical constitution, but the author considers the results of sufficient interest to warrant their publication.

EXPERIMENTAL

Exp. 1 : Phenylisocyanate and phenylacetylene (1 gm. each) were heated at 100-125° for 14 hours under exclusion of moisture and allowed to stand at room temperature for another three days. No reaction had taken place, as was demonstrated by the addition of aniline to afford carbanilide in good yield.

Exp. 2 : To phenylacetylene (1.5 g 1.5 mol) in dry ether (10cc) is added finely divided sodium (0.25g) in a flask fitted with an air condenser and a calcium chloride tube. After all the sodium had reacted (2 hours) the white solid is filtered rapidly at the pump, washed with a little dry ether, transferred back into the flask, covered with the solvent, cooled with ice and phenylisocyanate (1.5 g 1.3 mol) in ether added. Care was taken to see that no pieces of unreacted sodium remained before the filtration as otherwise there was a danger of the substance catching fire. The mixture was cooled before addition of the phenylisocyanate, to prevent the reaction becoming too violent. On the addition of this reagent the solid becomes yellow, the ether begins to boil and the solid assumes a brick-red colour, typical of the organometallics. After standing for 2 days, the substance was washed with dry ether and analysed after drying in the vacuum desiccator.

$$(2.228 \text{ g gave } 0.0685 \text{ g } Na_2SO_4. \quad \text{Found}: 9.7\% \text{ Na.})$$

This corresponds to a molecular weight of 237. When the reddish compound is worked up immediately, no crystalline solid can be isolated on hydrolysis, but on decomposing with a little alcohol after 36 hours, diluting with water and just acidifying with dilute hydrochloric acid, a yellowish mass is formed, which dissolves easily in chloroform, leaving a white substance (I), which crystallises in needles from alcohol or ethyl acetate m.p. 260° :

5.143 mg substance gave 14.246 mg CO_2 and 2.200 mg H_2O 2.917 mg substance gave 0.240 cc N_2 (30°, 752 mm).

8

'Found : C 75.7, H 4.8, N 9.2%. $C_{29}H_{21}O_3N_3$ requires C 75.8, H 4.6 N 9.2 %.

On evaporation the chloroform leaves behind a gummy residue, which crystallises in the form of yellow needles (II) from alcohol. After several recrystallisations the m.p. was constant at 201° :

5.479 mg substance gave 15.485 mg CO_2 and 2.330 mg H_2O.

2.830 mg substance gave 0.212 cc N_2 (29°, 753 mm).

0.226 mg substance in 4.130 mg camphor : $\triangle = 7.0°$.

0.228 mg substance in 4.698 mg camphor : $\triangle = 6.3°$.

Found : C 77.2, H 4.8, N 8.4% Mol. wt. 313, 308.

$C_{22}H_{16}O_2N_2$ requires C 77.1, H 4.7, N 8.2%, Mol. wt. 340.

In four experiments carried out in identical conditions, but using 2.0 g of phenylacetylene, instead of 1.5 g in order to facilitate the formation of sodium acetylide, the average yields of substances (I) and (II) were 0.12 g and 0.19 g respectively.

Further experiments were made with varying amounts of sodium phenylacetylide and phenylisocyanate :

Exp. 3 · The proportion of acetylide to phenylisocyanate was 1:2. Sodium (0.25 g) was reacted in the usual manner with phenylacetylene (1.5 g), and after separation of the acetylide and suspension in ether, an etherea solution of phenylisocyanate (2.4 g) was added to the cooled solution. The ether soon began to boil, but the colour change observed in previous experiments developed more slowly. On working up the mixture after standing 48 hours 0.2 g substance (I) was isolated. On taking up the chloroform soluble portion in alcohol, substance (II) did not appear to be present, but on standing a new substance slowly crystallised at the bottom of the vessel in yellowish brown cubes and prisms, which, after one further crystallisation, were pure : substance (III) m.p. 186°.

3.844 mg substance gave 10.900 mg CO_2 and 1.550 mg H_2O.

3.838 mg substance gave 0.284 mg N_2 (22°, 751 mm).

0.440 mg substance in 4.340 mg camphor :$\triangle = 10.0°$.

Found : C 77.3, H 4.5, N 8.5%, Mol. wt. 405.

$C_{22}H_{16}O_2N_2$ requires C 77.1, H 4.7, N 8.2% Mol. wt. 340.

Substance (III) is therefore an isomer of substance (II).

Exp. 4 : In this experiment the ratio of sodium acetylide to phenyliscocyanate was 2:1. Phenylacetylene (3 g) was reacted with sodium (0.5 g) and the acetylide formed treated with carbanil (1.2 g) in the usual manner. Though the colour change was observed, the ether failed to boil. On working up the mixture after 48 hours only a trace of a white compound was isolated on treatment with alcohol but as it was soluble in chloroform, it could not have been substance (I). From the mother liquors only a trace of substance (III) crystallised out. The rest was an intractable mass and could not be induced to crystallise.

In two further experiments, using 0.25 g sodium metal in each case, the ratio of sodium acetylide to carbanil was varied from 1:1.3 to 1:1.

The corresponding yields of substance (II) were 1.5 g and 1.0 g. In the second experiment 0.03 g of substance (I) could also be isolated, and substance (III) was not present.

Exp. 5 : Substance—(II) was treated with an excess of bromine in 15% chloroform solution. The excess of the halogen and the solvent were removed on the water bath and the residue recrystallised from alcohol in microcrystalline form (Substance IV). Yellow, m.p. 190-191.°
The mixed m.p. with substance (II) gave a large depression.

5.283 mg substance gave 12.175 mg CO_2 and 1.680 mg H_2O.

3.448 mg substance gave 0.206 cc N_2 (23°, 756 mm).

9.228 mg substance gave 4.345 mg AgBr.

Found : C 62.9 ,H 3.6, N 6.8, Br. 20.0%.

$C_{22}H_{15}O_2N_2$ Br requires C 63.0, H 3.6, N 6.7, Br. 19.1%.

Substances (1) and (III) were treated with bromine in the same manner but were recovered unchanged.

Exp. 6 : The crude sodio-derivative described in Experiment 2 was treated with an excess of benzoylchloride in ether. Sodium chloride was immediately precipitated. The reaction mixture was treated with cold sodium carbonate solution to decompose the excess of the reagent. The solid residue was recrystallised from alcohol and only unchanged substance (II) recovered.

Exp. 7 : The crude sodio-derivative was treated with methyl iodide both with and without a diluent (benzene). The mixture was warmed on the water bath and filtered from the sodium chloride formed. The filtrate could not be induced to crystallise, nor was it possible to prepare a crystalline bromination product. Attempts to isolate an oxidation product with potassium permanganate in acetone were also unsuccessful.

Exp. 8 : 0.5 g substance (II) was treated in 50 cc alcohol abs. with small quantities of sodium metal until the solution was decolorized, about 1.5 g metal being required. The mixture was diluted with water, neutralized with hydrochloric acid and evaporated to dryness. Attempts to obtain a crystalline product were unsuccessful.

Exp. 9 : Attempts to prepare the phenylcarbamate of 4-oxy-2-phenyl-quinoline : The quinolinol was prepared according to Knorr (Annalen, 1888, 245, 378).

4-oxy-2-phenyl-quinoline (0.3 g—,m. p. 254°) was heated with phenylisocyanate (0.2 g) in 5 cc toluene at 130° for 10 hours, cooled and the crystals washed with the cold solvents. M. p. 245° and after one recrystallisation from alcohol, 254°. In a second experiment phenylquinolinol (0.23 g) was heated in a closed tube with phenylisocyanate (1 g) for over 13 hours at 160-165°. The quinolinol was recovered unchanged.

SYNTHESES OF ANTI-LEPROSY DRUGS, PART I—A NEW SYNTHESIS OF ω-CYCLO-HEXYL UNDECYLIC ACID, AN ANA-LOGUE OF DIHYDROHYDNOCARPIC ACID

By

Miss B. C. Pandya, K. S. Nargund

AND

K. V. Bokil

INTRODUCTION

IT is well known that chaulmoogric acid (I) and hydnocarpic acid (II) are the best remedies, so far known, for leprosy. These drugs, how-ever, are known to be intensely toxic and are not quite specific against the disease ; the course of treatment with them is required to be prolonged considerably—sometimes from one to two or more years. They, therefore, leave much to be desired. Attempts have been made by a number of workers to impi ove upon the bactericidal properties of these drugs by (*i*) either converting them into suitable other derivatives, or (*ii*) synthesising altogether new compounds. Adams *et al* have shown that the introduction of cyclohexyl group in the above compounds enhances their bactericidal activity in vitro. Thus they synthesised a series of compounds, analogous to dihydrohydnocarpic and dihydro-chaulmoogric acids, containing cyclohexyl group instead of cyclopentyl in the *w*-position ; it was shown that the activity, in vitro, of the corres-ponding compounds in cyclohexyl series was greater than that of the cyclopentyl analogues. (J.A.C.S. 1926, *48*, 2387 ; *ibid.*, 1928, *50*, 1505.) They have also synthesised various substituted acetic acids and it was shown that the compound $C_6 H_{11} (CH_2)_2 —\underset{COOH}{\overset{CH-C_8}{}}H_{17}$ possesses one and a half times the bactericidal activity—in vitro—possessed by any of the natural drugs so far in use. (J.A.C.S. 1927, *49*, 2936 ; *ibid.*, 1929, *51*, 1262-1264.)

It was, therefore, thought that if Δ^2-cyclopentene group in compounds (I) and (II) was replaced by Δ^2-cyclohexene group the bactericidal properties of such compounds should increase proportionately.' The synthesis of these compounds on the lines of the methods used by Adams *et al* (various papers in J.A.C.S. from 1925 onwards) and Perkins and Cruz (J.A.C.S. 1927, *49*, 1070)—for the preparation of Δ^2-cyclopentene

compounds of (I) and (II) type, would obviously be not possible.. Recently a new method has been developed (Bokil and Nargund, Bomb. Univ. Jour. 1937, VI, (2), 93 ; Proceed. Ind. Acad. Sci. 1941, XIII, 233) which lends itself excellently for the preparation of these compounds. In the course of the preparation of Δ^3-cyclohexene analogue of hydnocarpic acid, *w*-cyclohexyl undecylic acid—an analogue of dihydrohydnocarpic acid—has been synthesised and described in the present paper. Hiers and Adams (J.A.C.S. 1926, *48*, 1092) synthesised the same by a method which is comparatively too lengthy.

Ethyl cyclohexanone-2-carboxylate was condensed, in the form of its potassium salt, with ethyl *w*-bromo undecylate giving the keto-diester (III) which on hydrolysis with concentrated hydrochloric acid gave a keto acid ester (IV). When boiled with methyl alcoholic caustic potash, the acid ester was not completely converted into the uibasic acid (V). The original keto-diester (III) under alkaline hydrolysis also gives a mixture of the acid ester (IV) and the dibasic acid (V). This mixture on distillation under reduced pressure gave cyclohexanone-2-*w*-undecylic acid (VI) as the first fraction, slightly contaminated with the acid ester (IV). After purification from ether and petrol, the ketonic acid (m.p. 61°-62° ; semicarbazone m.p. 134°-135°) was reduced by Clemmensen's method to the required *w*-cyclohexyl undecylic acid (VII) (m.p. 57°-58°). Hiers and Adams (loc. cit.) give the m.p. 58°-59°. Its ethyl ester and the amide (m.p. 107°-108°)—not described by the above authors—are also prepared.
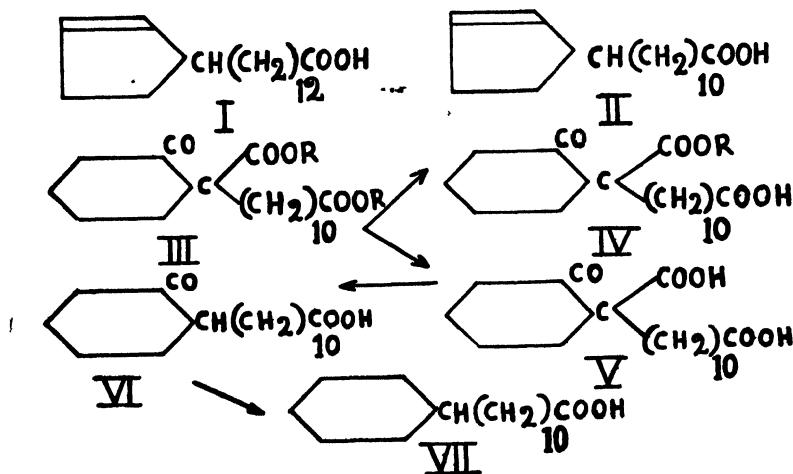
EXPERIMENTAL

Ethyl cyclohexanone-2-carboxylate—was prepared by the following modification of the method of Kotz and Michel (Annalen, 1906, *348*, 91-96).

Sodium ethoxide was prepared from 23 gms. sodium and 300 c.c. absolute alcohol, and the solution cooled in a freezing mixture. A mixture of cyclohexanone (100 gms.) and ethyl oxalate (150 gms.) was added and the whole mixture was left over night.. It was then poured

over crushed ice and the compound recovered in the usual way. Ethyl cyclohexanone-2-glyoxalate thus produced was heated to $150°$-$160°$ under moderately low pressure until the evolution of carbon monoxide was complete ; the residual liquid was then distilled under reduced pressure—b.p. $108°$-$112°$ at 12 mm. pressure. (Yield 80-85% of the theory.)

Ethyl w-bromo undecylate :—*w*-bromo undecylic acid was prepared from the redistilled undecylenic acid (of B.D.H. quality) by the petroleum ether method of Perkins and Cruz (J.A.C.S. 1927, *49*, 1073). It was esterified as described by Bokil and Nargund (Bomb. Univ. Jour. 1937, VI, 2, 95.)

Ethyl cyclohexanone-2-carboxylate-2-w-undecylate :—(III) Ethyl cyclohexanone-2-carboxylate (23 gms.) in dry benzene (200 c.c.) was treated with powdered potassium (5 gms.) ; the metal quickly dissolved giving a red coloured solution. After heating the mixture on water bath for half an hour, ethyl *w*-bromo undecylate (35 gms.) was added and the mixture heated on boiling water bath for eight hours. Preliminary experiments showed that the reaction was still quite incomplete ; the flask was, therefore, sealed and heated by immersing under boiling water for eight hours. The contents of the flask were decomposed by water, acidified and the product recovered in the usual way—crude yield 56 gms. This was distilled under reduced pressure when three fractions were collected—Fraction I, up to $140°/13$ mm.—8 gms. Fraction II, up to $240°/13$ mm.—10 gms. (mostly bromo-ester). Fraction III, between $250°$-$270°/13$ mm.—23 gms. (yield 50% of the theoretical). The last fraction was redistilled and the liquid passing over between $260°$-$265°/13$ mm. (20 gms.) was analysed. $D_4^{34}=1.0000$, $N_4^{34}=1.4618$. It does not give a semicarbazone. (Found C=69.6, H=9.7 per cent ; $C_{22}H_{38}O_5$ requires C=69.1, H=:9.95 per cent.)

Acid hydrolysis—cyclohexanone-2 carbethoxy-2-w-undecylic acid:—The ester (8 gms.) was boiled with concentrated hydrochloric acid (100 c.c.) for twelve hours and the acid was recovered in the usual way. When distilled under reduced pressure the acid passed over between $260°$-$265°/$ at 3 mm.—a thick liquid which becomes semisolid at $O°$; $N_D^{34}=1.4721$. (Found C=67.4, H=9.8 per cent ; Eq. wt.=353.4 ; $C_{20}H_{34}O_5$ requires C=67.8, H=9.6 per cent. ; Eq. wt.=354.)

Alkaline hydrolysis—preparation of cyclohexanone-2-w-undecylic acid:— (VI) The ester (III) (25 gms.) was hydrolysed by boiling with 20% methyl alcoholic caustic potash (12 gms. KOH) ; the acid recovered in the usual way gave an equivalent weight varying between 197 to 207— evidently a mixture of mono and dibasic acid. As the separation of the two could not be properly effected, the mixture was first heated at moderately low pressure until evolution of CO_2 stopped, and then distilled under reduced pressure—the fraction passing over between $240°$-$260°/10$ mm. solidified immediately ; (10 gms.) ; the higher fraction up to $280°$ partially solidified and contained some limpid mass. The solid acid was soluble in cold methyl and ethyl alcohol, benezene, chloroform acetone and ethyl acetate ; and moderately soluble in petrol. The limpid part of the acid (possibly acid ester) was much more insoluble in petrol and thus can be separated from the solid. The solid was crystal-

lised from petrol—containing a little ether—at 0°C in the form of microscopic plates—m.p. 61°-62°; the semicarbazone was prepared in the usual way (heating on water bath for a few minutes and cooling) and crystallises from alcohol in granules m.p. 134°-135°. It was esterified by the Fischer Speier method—the ester distilling over 210°-215°/3 mm.; $D_2^{32} = 0.9742$; $N_D^{32} = 1.4592$; the acid was analysed. (Found C=71.8 H=10.5 per cent; Eq. wt.=283.3; $C_{17} H_{30} O_3$ requires C=72.3, H=10.6 per cent; Eq. wt.=282.)

w-cyclohexyl undecylic acid :—(VII) A mixture of the above keto acid (9 gms.), amalgamated zinc (prepared from zinc—40 gms.) and concentrated hydrochloric acid—sp. gr. 1.19—(100 c.c.) was boiled for eight hours on sand bath. The solid was filtered off, washed and dried—m.p. 52°-53°; it was recrystallised thrice from 80% alcohol at 0°C—short leafy plates m.p. 57°-58°. It was esterified by the Fischer Speier method and the ester distilled—b.p. 193°-195°/3 mm.; $D_4^{33} = 0.9026$; $N_D^{33} = 1.4540$. The acid was analysed—(Found C=75.7, H=12.4 per cent.; Eq. wt.=267.8; calculated for $C_{17} H_{32} O_2$. C=76.1, H=12.3 per cent.; Eq. wt.=268).

The amide was prepared by the following method :—A mixture of acid (1 gm.), sodium dried petrol (15 c.c.) and phosphorustrimchloride (0.6 gms.) was heated on water bath for twenty minutes and the mixture poured, drop by drop, in 50 c.c. of concentrated ammonia solution, cooled to 0° in a freezing mixture. The slimy mass was filtered off and dried to expel petroleum ether, extracted with ether and ether removed; the residue was recrystallised twice from 95% alcohol—granules m.p. 107°-108°. (Found N=5.1 per cent.; $C_{17} H_{33} ON$ requires N=5.2 per cent.)

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SYNTHESES IN THE CHAULMOOGRIC ACID SERIES, PART IV—SYNTHESIS OF dl—Δ^2—CYCLOPENTENE-β-PROPIONIC ACID—A NEW HOMOLOGUE OF CHAULMOOGRIC ACID

By

K. V. BOKIL AND K. S. NARGUND

INTRODUCTION

IN Part II of this series (Proceed. Ind. Acad. Sci. 1940, XI, 409) reference was made to the work of Cole and Cardoso (J.A.C.S. 1939, 2349) who claimed to have isolated a whole series of lower homologues, of chaulmoogric acid—with even number of carbon atoms in the side chain—in the mixed fatty acids obtained from hydnocarpus wightiana oil. Thus along with chaulmoogric ($C_{18} H_{32} O_2$) and hydnocarpic ($C_{16} H_{28} O_2$) acids, they have isolated (*i*) alepric acid ($C_{14} H_{24} O_2$), (*ii*) aleprylic acid ($C_{12} H_{20} O_2$), (*iii*) aleprestic acid ($C_{10} H_{16} O_2$) and (*iv*) aleprolic acid ($C_6 H_8 O_2$) ; the synthesis of the last named acid-Δ^2-cyclopentene carboxylic acid—has already been described by the present authors in Part II (*loc. cit.*). The presence of the missing member ($C_8 H_{12} O_2$)-Δ^2-cyclopentene-β-propionic acid—in the H. Wightiana oil was indicated by the American authors, but it was not isolated by them. The synthesis of this compound is now accomplished and forms the subject matter of the present paper.

Noller and Adams (J.A.C.S. 1926, *48*, 2445) reduced the ester of Δ^2-cyclopentene acetic acid and the resulting alcohol was converted into the bromide ; they do not, however, seem to have proceeded further for the preparation of the above acid. It was at first thought possible to synthesise the acid by malonic ester synthesis, using the bromo-compound that could be obtained from the alcohol produced by the reduction of Δ^2-cyclopentene carboxylic ester. This ester on reduction gave an alcohol (b.p. 57°/10 mm.; p-nitrobenzoate m.p. 36°-37°) which, however, proved to be a Δ^1-compound, as it was found to be identical with one obtained from the corresponding Δ^1-ester.

The synthesis of Δ^2-cyclopentene β-propionic acid is represented by the following scheme of reactions :—
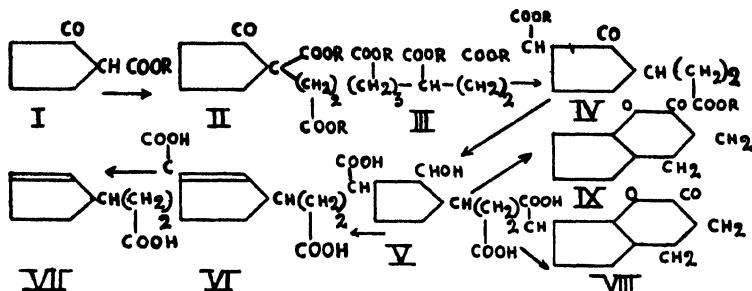
Ethyl cyclopentanone-2-carboxylate (I)—in the form of its sodium salt—was condensed with -β-iodo propionic ester, giving ethyl cyclopentanone-2-carboxylate-2-β-propionate. (II—F. E. King, J.C.S. 1935, 982 ; Cook and Linstead, *ibid.*, 1934, 953-954.) The keto diester was decomposed with very concentrated alcoholic caustic potash giving γ-carboxy suberic acid (III) along with a little acid ester which can be separated by ether. The acid ester could be completely changed into the tribasic acid by boiling with concentrated hydrochloric acid. The tribasic acid was converted into the normal ester by the silver salt method. The same ester could be obtained by heating the keto diester (II) with sodium ethoxide in absolute alcohol ; but the yield of the pure ester was not found to be quite satisfactory. Ethyl γ-carbethoxy suberate was converted by Dieckmann's method into ethyl cyclopenta-none-2-carboxylate 5- β-propionate (IV) with a much better yield than that claimed by Cook and Linstead (*loc. cit.*). The keto diester (IV) was then reduced (large excess of sodium amalgam) to the corresponding hydroxy compound, and the free hydroxy acid (V) was dehydrated by boiling with acetic anhydride. The dehydration product was found to be a mixture of four different compounds, the separation of which was effected in the following way :—Treatment with sodium carbonate solution left a small quantity of a neutral lactone (possibly IX) which could not be further investigated. The barium salts of the mixture of acids were then treated with boiling alcohol in which some quantity remained insoluble ; this yielded an acid which was found to be an unsaturated dibasic acid—(m.p. 128° 129°). The acids recovered from the soluble barium salts were further separated by the fractional dis-tillation of their ethyl esters, the lower boiling portion (b.p. 90°-92°/7 mm.) gave dl-Δ^2-cyclopentene-β-propionic acid on hydrolysis (b.p. 127°-129°/7 mm.). The higher boiling portion of the ester yielded a small quantity of an acid which appeared to be a lactonic acid (pro-bably VIII) which could not be completely investigated owing to want of material.

EXPERIMENTAL

Cyclopentanone-2-carboxylate-2-β-propionate :—Ethyl cyclopentanone-2-carboxylate (145 gms.) was converted into sodium salt with powdered sodium (21.3 gms.) in one litre of dry benzene ; on cooling ethyl-β-iodo ·

8 (a)

·propionate (208 gms.) was added with shaking, and the whole heated on boiling water bath for 10 hours. Ice water was added on cooling and the product worked up in the usual way—yield 170 gms.; b.p. 170°/10 mm. (73% of the theoretical) King (*loc. cit.*) gives 68% yield b.p. 172°/12 mm.; Cook and Linstead (*loc. cit.*) give 75% yield, b.p. 189°/18 mm. ·

γ-carboxy suberic acid :—The above keto diester—in lots of 10 gms. each—was digested with a concentrated solution of alcoholic potash (22 gms. contained 7.5 gms. KOH) on boiling water bath. All the lots were mixed together, some water added, alcohol distilled off and the alkaline solution extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid under cooling and the liquid extracted three times with ether ; ether was removed without drying and the residual mass dried in a vacuum desiccator—yield 135 gms. of a somewhat sticky solid (93% of the theoretical). The product was purified from a mixture of ether and petrol—a white solid m.p. 110°-111° ; (85 gms.)—(Cook and Linstead (*loc. cit.*) give m.p. 111°). Evaporation of ether left a jelly like mass (45 gms.)—an acid ester—which was converted into the solid tribasic acid by boiling with two volumes of concentrated hydrochloric acid. The mineral acid was removed under reduced pressure and the residue dried in a vacuum desiccator over caustic potash (32 gms.). The over all yield was, therefore, 83.5%. (Found C=49.3, H=6.6 per cent ; Eq. wt. 72.3 ; Calculated for C_9 H_{14} O_6—C=49.5, H=6.4 per cent. ; Eq. wt. 72.6.)

Ethyl γ-carbethoxy suberate :—The usual Fischer-Speier method gave a low yield of the normal ester which was, therefore, prepared by the silver salt method—110 gms. of the acid gave 130 gms. of the ester—b.p. 200°-205°/11 mm. (Cook and Linstead (*loc. cit.*) give b.p. 186°/9 mm.) $D_4^{34} = 1.0530$, $N_D^{34} = 1.43962$. (Found C=59.3, H=8.5 per cent ; Calculated for C_{15} H_{26} O_6—C=59.6, H=8.6 per cent.)

Ethyl cyclopentanone-2-carboxylate-5-β-propionate :—The above ester (120 gms.) benzene (350 c.c.) and sodium (10 gms.—powdered) were heated under reflux on a boiling water bath till the whole of the sodium went into solution. Water was then added, acidified and the product worked up in the usual way :—crude yield 100 gms. It gave an intense bluish violet colouration with alcoholic ferric chloride. The substance decomposes considerably during distillation, and only 55 gms. of a colourless oil was obtained over a range of 140°-200°/12 mm. On redistillation two fractions were collected ; fraction I—b.p. 150°-160°/12 mm.—15 gms., and fraction II—b.p. 175°-185°/12 mm.—25 gms. Both give ferric chloride reaction and both have almost the same refractive index, but different densities.—Fraction I—$D_4^{35} = 0.9503$; $N_D^{35} = 1.45257$; Fraction II—$D_4^{35} = 0.9810$; $N_D^{35} = 1.45287$. Both fractions gave the same semicarbazone—m.p. 154°-155°. It was subsequently observed that the low boiling gradually passes into the higher boiling portion during redistillation ; the two fractions, therefore, appear to be sterio-isomeric substances. (*cf.* P. C. Guha and G. D. Hazara, J. Ind. Chem. Soc. 1940, 107). Cook and Linstead (*loc. cit.*) got only 2.2 gms. of this substance from 20 gms. of the triester boiling at 186°/20 mm. (Found C=61.4, H= 8.0 per cent ; calculated for C_{13} H_{20} O_5, C= 60.9, H=7.8 per cent.)

Ethyl cyclopentanol-2-carboxylate-5-β-propionate :—The above keto ester (8 gms.) in 80% alcohol (70 c.c.) was treated with 600 gms. of 3.5% sodium amalgam, during 24 hours, in a strong current of CO_2. The end of the reaction was indicated by the non-appearance of the colour with ferric chloride. The alcoholic solutions from five such lots were mixed and alcohol removed under reduced pressure,—crude yield 28 gms. It could not be distilled and hence was not analysed.

The free hydroxy acid :—(20 gms.) obtained by the cold hydrolysis of the above ester, was a thick liquid with a strong fatty acid smell ; it could not be purified by distillation and, therefore, was not analysed.

Dehydration of the hydroxy dibasic acid :—Hydroxy acid (20 gms.) and acetic anhydride (30 c.c.) were kept just simmering on a sand bath under reflux air condenser for three hours ; the anhydride was removed under reduced pressure at the boiling water bath temperature and the last traces removed by keeping over solid caustic potash under vacuum. It was then taken up with ether, washed with a little water, dried over anhydrous sodium sulphate and ether removed ; the residue—a thick reddish liquid—was again dried in vacuum (yield 18 gms.). It readily decolourises bromine in chloroform. When treated with a concentrated solution of sodium carbonate a small quantity (0.5 gm.) remained insoluble which was extracted with ether. The substance showed lactonic behaviour and absorbed bromine in chloroform ; the amount being small, it was not further investigated.

The mixture of acids was recovered from the alkaline solution and neutralised, in alcoholic solution, with barium hydroxide (litmus test). The barium salts were obtained by evaporating the liquid to dryness, and then boiled with 95% alcohol ; the insoluble salt (A) was filtered off and the soluble barium salt was recovered (B) by evaporating the alcohol.

Isolation of Δ^2-cyclopentene-β-propionic acid :—The soluble barium salt (B) was decomposed, and the titration of the recovered acid (6.5 gms.) indicated it to be a mixture, probably containing some lactonic acid. The mixture of acids was, therefore, converted into ethyl ester through the silver salt and fractionated. The fraction boiling at 90°-92°/7 mm. (4 gms.) rapidly decolourised bromine in chloroform. $D^{25}_4 = 0.9910$; $N^{25}_D = 1.45356$. (Found C=71.6, H=9.4 per cent ; C_3 H_{16} O_2 requires C=71.4, H=9.5 per cent.)

The above ester was hydrolysed by alcoholic caustic potash in cold and the free acid obtained was distilled ;—b.p. 127°-129°/7 mm. (2.5 gms.) It is a thick syrupy liquid which forms an emulsion with water. $D^{30}_4 = 0.9997$, $N^{30}_D = 1.47007$. (Found C=68.9, H=8.5 per cent. Eq. wt. = 140.7 ; C_8 H_{12} O_2 requires C=68.6, H=8.6 per cent. ; Eq. wt. = 140).

The higher fraction remaining in the distilling flask was too small for distillation ; it was hydrolysed and the free acid showed lactonic behaviour. The quantity, however, was too small to be further investigated.

The above unsaturated acid slowly decolourised bromine in chloroform. The iodine value (Hanus) was found to be very low under the

usual conditions—23.5 only ; (for the ester it was only 35). There was no liberation of iodine at the end of the titration (*cf.* Bokil and Nargund Proceed. Ind. Acad. Sci. 1940, XI, 410). It appeared, therefore, that the low values might be due to some inhibiting effect. This proved to be the case, for the iodine values increased with time and the quantity of the Hanus solution. Thus by using three times the usual quantity of the Hanus solution, and increasing the reaction period to ten hours, the value obtained for the acid was 179.8 (calculated=181.5) ; and that for the ester was 149.2 (calculated=151.5).

Isolation of the unsaturated dibasic acid (VII) :—The insoluble barium salt was decomposed and the recovered acid dried in vacuum. Treatment with a little cold ether removed the sticky matter, leaving a white solid m.p. 126°-127°. It was insoluble in benzene, petrol and chloroform ; when purified from ether-petrol mixture it melted at 128°-129°. (Found C=58.3, H=6.7 per cent ; Eq. wt.=91.3 ; $C_9 H_{12} O_4$ requires C=58.7, H=6.5 per cent ; Eq. wt.=92.)

Δ^1-*cyclopentene carbinol* :—Ethyl Δ^2-cyclopentene carboxylate (7gms.) and absolute alcohol (80 c.c.) were taken in a flask fitted with a reflux condenser carrying a calcium chloride tube ; the flask was heated on an oil bath till alcohol just began to boil. Flame was then removed and sodium (5 gms.) was added (in lots) as quickly as possible so as to keep the liquid boiling all the while. When the vigorous reaction had subsided, temperature of the bath was raised to 140° until all the sodium had completely dissolved. After cooling water (15 gms.) was added and the solution boiled ; 100 c.c. of water are now added to the hot liquid and alcohol distilled off. On cooling an insoluble oil separated which was extracted with ether, washed with water, dried over anhydrous potassium carbonate and ether removed. A yellowish-red mobile liquid was obtained (2 gms.) which possessed a strong smell of amyl alcohol—b.p. 57°/10 mm. $D_4^{35}=0.9287$, $N_D^{35}=1.45237$. Its p-nitrobenzoate crystallised from dilute methyl alcohol, at low temperature, in granules m.p. 36°-37°. (Found C=73.6, H=10.0 per cent ; $C_6 H_{10} O$ requires C=73.5, H=10.2 per cent.)

The Δ^1-ester was reduced in a similar way and the p-nitro-benzoate of the resulting alcohol melted at 36°-37° ; it did not depress the melting point of the p-nitro-benzoate of the first alcohol.

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AN ATTEMPT AT THE DIRECT SYNTHESIS
OF β—SUBSTITUTED CINNAMIC ACIDS

By

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IN an attempt to prepare β-β-disubstituted glutaric acids according to the method of Dixit and Gokhale (Bom. Univ. Jour. 1934, III, 80) a new compound was recently isolated (Vyas and Bokil, Rasa-yanam, 1939, 195) from the condensation of acetone-dicarboxylic acid with anisole in presence of 80% sulphuric acid. It was proved to be β-β-disubstituted butyric acid by its synthesis, first from the condensation of acetoacetic ester with anisole, and secondly, by the addition of anisole to p-methoxy-β-methyl cinnamic acid—both under the influence of 80% sulphuric acid. (Vyas and Bokil, Rasayanam, 1939, 198-200.) This definitely indicated the formation of substituted cinnamic acid as the intermediate product in the first type of synthesis. α-substituted acetoacetic ester condenses in a similar way; but α-α disubstituted ester does not at all condense. The use of dilute sulphuric acid solution as condensing agent in condensations involving the use of acetoacetic ester has, as far as the authors know, not been noted before.

It was, therefore, proposed to determine the conditions under which the intermediate cinnamic acids could be isolated. Acetoacetic ester was condensed with phenolic ethers under the influence of different concentrations of sulphuric acid, at the ordinary temperature, over different periods of time and using different quantities of reacting substances (cf. experimental). All the experimental evidence showed that concentrations of sulphuric acid lower than 80% have little or no effect in bringing about condensation. 80% acid is very effective, but produces either substituted butyric acids (A) or their esters or both, depending upon the molecular proportions of the reacting substances used. In addition, a trace of another acid (B) is obtained which is produced somewhat in a larger quantity—along with esters and acids of (A) type —when 85% sulphuric acid is used as condensing agent. This latter strength of sulphuric acid also produces sulphonated acids (C) which

are the main products of condensation when 90% sulphuric acid is used as condensing agent. The (B) type acids appear to be addition products of a molecule of acetoacetic ester with the intermediate cinnamic acids or their esters, and the determination of the exact nature of these is under investigation. The sulphonated acids also seem to be the result of the addition of sulphuric acid to the intermediate unsaturated compounds, and this peculiar phenomenon is also under investigation. In no case could, however, even a trace of the expected cinnamic acids or their esters be isolated under any conditions, presumably due to the rapid addition of the phenol ethers or—when these are more or less prevented from adding—the acetoacetic ester to the intermediate cinnamic acids or their esters. This latter addition is interesting since the Michael addition of the sodium salt of acetoacetic ester (or malonic ester) to β-substituted cinnamic esters is shown to be entirely prevented. (Schroeter, Ber. 1907, 1591 ; Phalnikar and Nargund, Bom. Univ. Jour. 1936, V, 2, 105).

The above findings are contrary to the observation made by Limaye (Rasayanam, 1939, 186) of having obtained small quantities of β-substituted cinnamic acids from the condensation of acetoacetic ester with anisole and phenetole, for which no details are given.

Benzoyl acetic ester is not found to condense under the above conditions. The ease with which the phenol ethers can add to different β-substituted cinnamic acids is also being studied.

EXPERIMENTAL

General procedure for condensation and working up of the products :

The acetoacetic ester and phenol ether in various molecular proportions are weighed out in a flask and 80-85 gms. of sulphuric acid of different strength is slowly added under cooling. The mixture is then kept over a definite time period with occasional shaking ; in some cases frequent shaking was found necessary. The reaction mixture is then poured over crushed ice with shaking and (a) allowed to stand for a few hours for complete disintegration when 80% sulphuric acid is used ; (b) when, however, 85% or 90% sulphuric acid is used the ice-cold acid liquid is decanted from the separated jelly-like mass, otherwise the sulphonated acids formed go into solution on standing and are lost. The jelly like reaction product is then taken up with ether in which the sulphonated acid—if formed—remains insoluble, the ether solution washed with sodium bicarbonate solution, then with water, dried and the neutral substance recovered. The alkaline layer is acidified and the acid recovered and purified in the usual way. Sometimes the

β-β-disubstituted butyric acids are found to be much more insoluble in ether and thus get separated during ether treatment.

In the preliminary experiments anisole was condensed with aceto-acetic ester in the presence of 65%, 70%, 75%, 80%, 85%· and 90% sulphuric acid ; the results obtained are given in the following tabular form :—

%H_2SO_4, and its quantity	Acetoacetic ester	Anisole	Time period	Products formed
65%, 85 gms.	13 gms. (1 mol.)	11 gms. (1 mol.)	16 hours	No reaction
			72 hours	No reaction
70% ,,	13 gms. (1 mol.)	11 gms. (1 mol.)	16 hours	A little (A) type acid formed
70% ,,	26 gms. (2 mol).	do.	72 hours	1 gm. acid (A) 2 gms. its ester
75% ,,	13 gms. (1 mol.)	do.	16 hours	2 gms. acid (A)
75 ,,	26 gms. (2 mol.)	do.	24 hours	2.5 gms. acid (A) 5 gms. its ester
80% ,,	13 gms. (1mol.)	do.	16 hours	3 gms. acid (A) 3 gms. its ester
80% ,,	do.	do.	48 hours	8 gms. acid (A) 0.5 gms. acid (B) type
80% ,,	26 gms. (2 mol.)	do.	16 hours	2 gms. (acid A) type 10 gms. its ester 1 gm. acid (B) type
85% 80 gms.	13 gms. (1 mol.)	do.	10 hours	2 gms. acid mixutre 6 gms. mixture of esters (A & B) 7 gms. sulphonated acid (C)
85% ,,	26 gms. (2 mol.)	do.	do.	3 gms. acid mixture 12 gms. mixture of esters 3 gms. sulphonated acid (C)
90% ,,	13 gms. (1 mol.) .	do.	do.	A little acid (B) type 4 gms. sulphonated acid (C)
90% ,,	26 gms. (2 mol.)	do.	do.	Same as above with a little ester

. , The ester of the acid (A) mentioned above—ethyl β-β-di (p-methoxy phenyl)-butyrate—distilled between 230°-240°/ 15 mm. pressure methyl ester distills between 250°-255°/18 mm. ; both are thick sirupy liquids. Anilide of the acid has m.p. 147°-148° ; p-toluidide m.p. 144°-145°.

From the above table it is clear that sulphuric acid of 80% and 85% strength gives larger quantities of reaction products. For our present study, however, sulphuric acid of 80% strength is used in the other condensation reactions with (a) phenetole, (b) o-cresolmethyl ether,. (c) m-cresol methyl ether, and (d) p-cresol methyl ether.

(a) *Condensation with phenetole—formation of* β-β-di (*p-ethoxy phenly*) *butyric acid :*—Phenetole (12 gms.), acetoacetic ester (13 gms.) and 80% sulphuric acid (80 gms.) were mixed and kept for 27 hours. The reaction product was decomposed and worked up in the usual way ; 1 gm. of the crude acid and 10 gms. of crude ester were obtained. The ester distills between 250°-270°/8 mm. ; methyl ester b.p. 250°-265°/8 mm. The esters give a green fluorescence. On hydrolysis with alcoholic caustic potash a limpid acid is obtained which solidifies on keeping in vacuum over solid caustic potash and solid paraffin, for several days, m.p. 60°-62°. It does not crystallise well from any solvent ; (Found $C=72.4$, $H=7.6$ per cent ; Eq. wt.$=330. 1$; $C_{20} H_{24} O_4$ requires $C= 73.1$, $H=7.3$ per cent ; Eq. wt.$=328$). Anilide m.p. 135°.

Synthesis of the acid :—p-ethoxy-β-methyl cinnamic acid (Schroeter, Ber. 1908, 10) (10 gms.) was mixed with 80% sulphuric acid (40 gms.) and phenetole (6 gms.) was added ; after shaking and standing for two hours the proudct was worked up in the usual way. The purified substance immediately solidified in vacuum, m.p. 60°-62° ; mixed melting point remains unchanged.

(b) *Condensation with o-cresol methyl ether—formation of* β-β-di—(*3-methyl-4-methoxy phenyl*) *butyric acid :*—o-cresol methyl ether (12 gms.), acetoacetic ester (13 gms.) and 80% sulphuric acid (80 gms.) were mixed and kept for 17 hours ; products—recovered in the usual way— consisted of a sticky acid (6 gms., a mixture of A and B types) and an ester (6 gms.). The ester was hydrolysed in cold and the dried ethereal solution of the acid allowed to evaporate in air ; crystalline solid with some sticky mass was obtained. The solid acid was separated by washing with a little cold ether and then crystallised from dilute alcohol— small plates, m.p. 131°-132°. The substance is not synthesised ; it gave the following results on analysis:—(Found $C=72.6$, $H=7.5$ per cent; Eq. wt.$=328.3$; $C_{20} H_{24} O_4$ requires $C=73.1$, $H=7.3$ per cent; Eq. wt.$= 328$). Anilide m.p. 141°-142°.

(c) *Condensation with m-cresol methyl ether :*—m-cresol methyl ether (12 gms.), acetoacetic ester (13 gms.) and 80% sulphuric acid (80 gms.) were mixed and kept for 18 hours ; the products recovered consisted of a sticky acid (1.5 gms.—B type) and a neutral compound (1 gm.)— long rhombic needles from ether, m.p. 132°-133°. This was identified as 4-7-dimethyl coumarin by mixed melting point method using an authentic sample prepared by heating 7-methyl coumarin-4-acetic acid ; (Fries and Volk, Annalen, 1911, *370*, 107).

(d) Condensation with p-cresol methyl ether :—p-cresol methyl ether (12 gms.), acetoacetic ester (13 gms.) and 80% sulphuric acid (80 gms.) were mixed together and kept over for 72 hours with occasional shaking, and then worked up in the usual way. A sticky acid (B type—3 gms.) and a neutral solid were obtained ; the solid crystallised from alcohol in needles, m.p. 150°-151° (2 gms.) With 85% sulphuric acid, a little larger quantity (4 gms.) of the neutral solid was obtained. This was identified as 4-6-dimethyl coumarin by its mixed melting point with an authentic sample prepared according to the method of Dey ; (J.C.S. 1915, 1636.)

ACTION OF THIONYL CHLORIDE ON β -NAPHTHOL AND 1:2-OXY-NAPHTHOIC ACID

By

J. W. AIRAN AND S. V. SHAH

THIS work is in continuation of the work by the authors (J. Univ. Bom., 1940, *9*, 115), in which it was reported that with thionyl chloride, under the conditions described there, β-naphthol gave only a plastic mass, and that 1 : 2 oxynaphthoic acid and 2 : 3-oxynaphthoic acid failed to react with thionyl chloride, the original acids being recovered.

The investigation with these three compounds was pursued further, when under the conditions described in the present paper, thioethers were obtained in the case of β-naphthol and 1 : 2-oxynaphthoic acid, whereas in the case of 2 : 3-oxynaphthoic acid a product is obtained which contains neither -OH nor -COOH groups, and which appears to be a mixture of a couple of compounds which is being investigated.

β-naphthol, with thionyl chloride, gave a thioether which was found to be identical with the one already obtained with sulphur dichloride, *viz.*, 2,2'-dihydroxy-dinaphthyl sulphide (*Ibid.*, p. 120).

The thioether obtained as a result of the interaction of thionyl chloride and 1 : 2-oxynaphthoic acid at 110°C was found to be identical with the one already obtained with sulphur dichloride, *viz.*, 3, 3'-dicarboxy-4, 4'-dihydroxy-dinaphthyl sulphide (*Ibid.*, p. 122). In this case it should be noted that :—

(*i*) H. Meyers (Mon., *22*, 790) treated 1:2-oxynaphthoic acid with thionyl chloride at 50°C, and obtained its acid chloride, (melting point 82-86°C).

(*ii*) Hirve, Jadhav, and Chakradev (J. Univ. Bom., 1937, *6*, 82) converted salicylic acid into esters before allowing it to react with thionyl chloride, lest the -COOH group be attacked by thionyl chloride.

But in the present investigation, the interaction of thionyl chloride and 1 : 2-oxynaphthoic acid was carried out without converting the acid into an ester, and it was found that the -COOH group remained unaffected.

Both the thioethers reported in the present paper gave acetyl derivatives which were identical with the acetyl derivatives of the corresponding

thioethers obtained with sulphur dichloride (*ibid.*, pp. 121 and 123 respectively). Thus in these two cases also the sulphur atom has entered the position which is ortho, in the case of the former, and para, in the case of the latter, to the -OH group.

EXPERIMENTAL

(The experimental part of this work was carried out by Mr. Airan alone.—*S. V.S.*)

2, 2'-dihydroxy-dinaphthyl sulphide (I)

β-naphthol (10 gms.) was dissolved in ether, and thionyl chloride (about 9 gms.) was added to it. Dry crystals of bismuth chloride were added as catalyser. The reaction mixture was kept overnight in a conical flask provided with a glass tube in a tight-fitting cork, the tube itself being drawn out into a fine capillary to keep out the moisture.

Next day, finding that no solid had fallen out, the mixture was poured in water, when only a plastic mass was obtained from which nothing could be recovered.   .

The same reaction was repeated, the flask this time being surrounded by ice, and thionyl chloride was added in small quantities at a time. The flask was then kept in a cold water bath overnight, and next day again finding that no solid had fallen out, the ether was evaporated. The residue left was treated with ether, in which now it did not dissolve. The yield was less than 20 per cent. The solid melted at 212°C. Its mixed melting point was 212°C with 2,2'-dihydroxydinaphthyl sulphide, melting point 212°C (Airan and Shah : J. Univ Bom., 1940, 9, 120). It gave the ferric chloride test for hydroxyl group.

Then the same reaction was carried out with the following modifications :—

Instead of ether benzene was used as medium. β-naphthol was not actually dissolved in benzene, but was maintained in suspension. The mixture was contained in a round bottom flask fitted with dropping funnel (top closed), and a capillary exhaust. The flask was held in a water bath which was heated just below the boiling point of benzene, and thionyl chloride was added, a few drops at a time. During the process, β-naphthol went into solution ; but within half an hour a solid mass began to fall out which was proved to be identical with the sulphide, m.p. 212°. The yield was about 30 per cent. Inspite of several recrystallizations this compound retains a slightly chocolate tinge. (Found : S,10.3 ; $C_{20} H_{14} O_2 S$ requires 10.07 per cent.)

Acetylation of Compound I (II)

Compound I was refluxed with acetic anhydride and the acetyl derivative was obtained in the usual manner. It melted at 198°C. Its mixed melting point also was 198°C with 2,2'-diacetoxy-dinaphthyl sulphide, melting point 198°C (*Ibid.*, p. 121).

3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide   (III)

1:2-oxynaphthoic acid (10 gms.) was taken in a distilling flask and bismuth chloride (0.2 gm.) was added as catalyser. The flask was fitted with a dropping funnel containing quite an excess of thionyl chloride. The flask was held in an oil bath and a little thionyl chloride was added only after the bath had attained the temperature of 110°C, at which it was maintained throughout. At each addition of thionyl chloride the flask was shaken thoroughly.

In this manner, within about 20 minutes the whole of the thionyl chloride was added. The escaping gases and the excess of thionyl chloride were led directly into the sink. The flask was kept in the bath till the reaction mixture was completely dry. The solid was then extracted with chloroform, in which it did not dissolve. It was then washed with hot carbon tetrachloride and also with ether. It melted at 265°C. Its mixed melting with 3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide, melting point 265°C (*Ibid.*, p. 122) was not depressed. It gave the ferric chloride reaction for hydroxyl group. The yield was about 30 per cent. (Found : S, 7.894 ; $C_{22} H_{14} O_6$ S requires 7.881 per cent.)

Acetylation of Compound III   (IV)

Compound III was acetylated in the usual manner by refluxing it with acetic anhydride. It melted at 151°C. Its mixed melting point with 3,3'-dicarboxy-4,4'-diacetoxy-dinaphthyl sulphide, melting point 151°C (*Ibid.*, p. 123) was undepressed.

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INTERACTION OF SULPHURYL CHLORIDE AND NAPHTHOL DERIVATIVES

By

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IN a former communication (J. Univ. Bom., 1940, *9*, 3 115), we had described the action of the chlorides of sulphur (sulphur dichloride and sulphur monochloride) and of an oxychloride of sulphur (thionyl chloride) on certain naphthol derivatives. Hence it was considered of interest to see how the other oxychloride of sulphur (sulphuryl chloride) would react with these naphthol derivatives.

Holmberg (Annalen, *359*, 81) found that with sulphuryl chloride mercaptans gave the corresponding disulphides :

$$2 \text{ R. SH} + SO_2 Cl_2 \longrightarrow R_2 S_2 + SO_2 + 2 \text{ HCl}$$
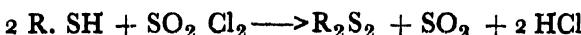
T. H. Durrnas (J.C.S., *121*, 44) found that the chlorinating action of sulphuryl chloride sometimes resembled that of chlorine and sometimes that of phosphorus pentachloride. It also acted as a dehydrating agent, its action in this case resembling that of sulphur t᾿ ioxide.

O. Silberrad (J.C.S., *1921*, 2029) found that in the presence of aluminium chloride, chlorination of benzene with sulphuryl chloride was brought about in a few minutes at ordinary temperature and that it was not necessary to heat the mixture in sealed tubes as was done by Tohl and Eberhard (Ber., *26*, 2941).

Armstrong and Rossiter (Chem. News, *59*, 225) obtained 1-chloro-2᾿ oxy-naphthalene by the interaction of β-naphthol and sulphuryl chloride by heating the mixture in carbon disulphide.

In the present investigation, 2-acetyl-α-naphthol, 1:2-oxynaphthoic acid, and 2:3-oxynaphthoic acid, as well as α-naphthol were allowed to react separately with sulphuryl chloride under no special conditions, except that dry crystals of bismuth chloride (0.2 gm.) were employed as catalyser. It was found that neither the -OH nor the -COOH was in any way affected by sulphuryl chloride, but that the -H atom para, in the case of 2-acetyl-α-naphthol, 1:2-oxynaphthoic acid, and α-naphthol, and ortho, in the case of 2:3-oxynaphthoic acid, to the -OH group was replaced by a chlorine atom.

The products in the following cases were obtained within a couple of minutes (whereas in the case of α-naphthol time was required) :—

2-acetyl-α-naphthol ; 1:2 and 2:3-oxynaphthoic acids.

The position of the chlorine atom in the case of the products obtained with 1:2 and 2:3-oxynaphthoic acids was ascertained as follows :—

The compound obtained with 1:2-oxynaphthoic acid and sulphuryl chloride was found to be identical with the compound obtained by H. Weil (Ber., *44*, 3061), melting point 229°,*C* by passing chlorine in an acetic acid solution of 1:2-oxynaphthoic acid, and which he named : 4-chloro-l-hydroxy-2- naphthoic acid.

Similarly, the compound obtained from 2:3-oxynaphthoic acid and sulphuryl chloride was found to be identical with 4-chloro-3-hydroxy-2-naphthoic acid prepared by Gradenwitz (Ber., *27*, 2622) by passing chlorine in an acetic acid solution of 2:3-oxynaphthoic acid (m.p. 230-233°*C*).

But in the case of the product obtained with 2-acetyl- α -naphthol, the position of chlorine was ascertained by analogy with 4-bromo-2-acetyl- α -naphthol (Hantzsch : Ber., *39*, 3097) as follows :—

Hantzsch treated 2-acetyl- α -naphthol with bromine and obtained 4-bromo-2-acetyl- α -naphthol, but Üllmann (Ber., *30*, 1468) had already obtained another bromo-derivative of 2-acetyl- α -naphthol in which the bromine atom had replaced an -H atom of the acetyl group.

Now, in order to see whether the chlorine compound obtained in the present investigation, contained the chlorine atom in the side chain, the compound was refluxed with sodium' hydroxide solution. On being acidified with nitric acid, a solid was obtained which contained chlorine, whereas the filtrate gave no test for chlorine. This indicated that the chlorine atom was not in the side chain. Hence the compound, by analogy with Hantzsch's bromo-compound, could be named: 4-chloro-2-acetyl- α -naphthol.

The chloro-compound obtained with α -naphthol and sulphuryl chloride was found to be identical with 4-chloro- α -naphthol (Kauffmann and Reverdin : Ber., *28*, 3052).

Thus in all these cases the in-coming chlorine atom entered 4-position, without in any way affecting either the -OH or the -COOH group, indicating that in these cases, sulphuryl chloride in its chlorinating action resembles chlorine.

Even when no catalyser was employed, the same products in all these cases, except in the case of α -naphthol, were obtained, the only difference being that of time.

EXPERIMENTAL

(The experimental part of this work was carried out by Mr. Airan alone.—*S. V.S.*)

4-chloro-2-acetyl- α -naphthol

To a saturated solution of 5 gm. of 2-acetyl- α -naphthol in ether was added sulphuryl chloride (2 c.c.) at room temperature, which was 32°*C.* Bismuth chloride was employed as a catalyser. Within a couple of

minutes a solid fell out. It melted at 116°C. It gave positive ferric chloride reaction. (Found : Cl=16.43 ; $C_{12} H_9 O_2 Cl$ requires 16.1 per cent.)

Identical product was obtained even without the catalyser, but after one hour of standing the reaction mixture had to be warmed in water bath before the substance could fall out.

4-chloro-2-acetyl-1-acetoxy-naphthalene

Compound I was refluxed for 8 to 9 hours with an excess of acetic anhydride and then the reaction mixture was poured in cold water. The solid obtained was crystallized from alcohol. It melted at 82°C. (Found : Cl, 13.93 ; $C_{14} H_{11} O_3 Cl$ requires 13.52 per cent.)

Its equivalent weight was calculated by refluxing the substance with an excess of standard potassium hydroxide solution, and then back-titrating with standard HCl.

(Found : Equivalent weight 251, required theoretically, 262.5.)

4-chloro-1-hydroxy-2-naphthoic acid

A saturated solution of 5 gms. of 1:2-oxynaphthoic acid was prepared in ether at the room temperature of 32°C. Bismuth chloride (0.2 gm.) was added as a catalyser. Then sulphuryl chloride (2 c.c.) was added, when almost at once a solid fell out which melted at 229°C. This compound gave a mixed melting point of 229°C with the compound prepared according to H. Weil's (Ber., 44, 3061) method, and which also had the melting point 229°C. It gave the ferric chloride test. (Found : Cl, 15.4 ; $C_{11} H_7 O_3 Cl$ requires 15.95 per cent.)

(Found : Equivalent weight 205.7, required theoretically, 222.5.)

Even in the absence of a catalyser identical product was obtained, but after about an hour.

4-chloro-1-acetoxy-2-naphthoic acid

Compound III was refluxed for a few minutes in an excess of acetic anhydride with a trace of concentrated sulphuric acid. Then the mixture was poured in cold water. The solid obtained melted at 102°C. (Found : Cl, 13.58 ; $C_{13} H_9 O_4 Cl$ requires 13.42 per cent.)

4-chloro-3-hydroxy-2-naphthoic acid

A saturated solution of 5 gms. of 2:3-oxynaphthoic acid was prepared in ether at the room temperature of 32°C, and bismuth chloride (0.2 gm.) was added as a catalyser. Then sulphuryl chloride (2 c.c.) was added, when almost at once a solid fell out. It melted at 230°-233°C (alcohol). This compound gave a mixed melting point of 232-233°C with the compound prepared according to Gradenwitz's (Ber., 27, 2622) method, and which also had the melting point of 230-233°C. It gave positive ferric chloride reaction. (Found : Cl, 16.14 ; $C_{11} H_7 O_3 Cl$ requires 15.95 per cent.)

(Found : Equivalent weight 221.1, required theoretically, 222.5.)

Even without the catalyser identical compound was obtained, but after about an hour.

4-chloro-3-acetoxy-2-naphthoic acid

Compound V was refluxed with acetic anhydride for a few minutes with a trace of concentrated sulphuric acid, and then was poured in cold water. The solid obtained melted at 186°C. (Found : Cl, 13.68 ; $C_{13} H_9 O_4$ Cl requires 13.42 per cent.)

4-chloro- α -naphthol

This compound was obtained by the interaction of 2 c.c. of sulphuryl chloride and 5 gms. of α -naphthol in ether. Bismuth chloride (0.2 gm.) was used as a catalyser. No solid fell out as in other cases, and hence the mixture was left overnight in a conical flask. Next day it was found that a solid had fallen out. It melted at 116-117°. Its acetyl derivative was prepared, which melted at 44°C. Both these compounds are known (Kauffmann and Reverdin : Ber. 28, 3052). They had obtained the chloro compound by boiling 4-chloro-naphthyl carbonate with alcoholic potash.

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PHENYL GLUTARIC ACIDS, PART III—
∝ ∝ DIPHENYL GLUTARIC ACID

By

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THE purpose of synthesising phenyl glutaric acids as well as the synthesis of ββ diphenyl and β phenyl β methyl glutaric acids has been reported in previous parts (Phalnikar and Nargund, Jour. Bom. Univ. 1936, Vol. V, Part II, page 105 ; *ibid*, 1937, Vol. VI, Part II, page 102). Ethyl diphenyl acetate did not react with ethyl β iodopropionate either in presence of sodium ethoxide or sodamide under any conditions. Diphenyl acetonitrile, however, readily reacted with ethyl β iodopropionate in presence of sodium ethoxide. The use of sodamide in the above reaction was less satisfactory. The isolation of ethyl γ cyano γγ diphenyl butyrate from the mixture of this with diphenyl acetonitrile presented some difficulty, which was got over by the observation that hydrolysis by dilute alkali in cold hydrolysed the ester group completely without affecting the cyano group so that the resulting γ cyano γγ diphenylbutyric acid could be easily isolated and purified from the unchanged diphenyl acetonitrile. Neither treatment with boiling concentrated hydrochloric acid for twenty-four hours nor boiling with alcoholic sodium hydroxide (30 per cent. solution) effected the hydrolysis of the cyano group in γ cyano γγ diphenyl butyric acid. Heating in a sealed tube with concentrated hydrochloric acid at 160-170° for six hours, however, hydrolysed it and gave a good yield of ∝ ∝ diphenyl glutaric acid which has been characterised by the usual derivatives.

∝ ∝ Diphenyl glutaric acid readily yielded an anhydride while ββ diphenyl glutaric acid did not give its anhydride under any conditions. The reason of this will be clear when the dissociation constants and the rates of hydrolysis of the esters and imides of these acids are determined —a work which is in progress in this laboratory.

EXPERIMENTAL

Diphenyl acetonitrile was prepared in an overall yield of 40 per cent from benzaldehyde through benzoin, benzil, benzilic acid, diphenyl acetic acid and diphenyl acetamide. No trace of it could be prepared from benzaldehydecyanohydrin, benzene and phosphorus pentoxide as claimed by Michael and Jenpretre (B. *25*, 1615).

γ Cyano γγ diphenyl butyric acid :—To a cold mixture of diphenyl acetonitrile (10 gms.) and sodium ethoxide prepared from sodium (1.2 gms.) absolute alcohol (12 c.c.) was added with stirring ethyl β iodopropionate (12 gms.). It was heated on water bath till it showed neutral reaction (2 hours). It was then cooled and a solution of 20 per

cent. sodium hydroxide (25 c.c.) was added and left over for 24 hours at room temperature. It was then diluted with water and the precipitated acetonitrile was filtered off and the filtrate on acidification gave γ cyano $\gamma\gamma$ diphenyl butyric acid. (Yield 10 gms.) It was soluble in ethyl and methyl alcohol, chloroform, ethyl acetate, hot benzene, hot acetic acid and insoluble in petrol. It crystallised in prisms from dilute alcohol m.p. 161-162°. Barium, calcium, lead and silver salts were insoluble in water. (Found : C, 76.8 ; H, 6.0 per cent. Eq. wt. 264.3. Ag in silver salt, 29.2 per cent. $C_{17} H_{15} O_2 N$ requires C, 77.0 ; H, 5.7 per cent. Eq. wt. 265. $C_{17}H_{14} O_2$ NAg requires Ag, 29.0 per cent.)

α α *Diphenyl glutaric acid :*—γ cyano $\gamma\gamma$ diphenyl butryic acid (5 gms.) was heated in a sealed tube with concentrated hydrochloric acid (25 c.c.) at 160-170° for six hours. The product obtained was purified by sodium carbonate treatment to free it from some neutral impurities. It was soluble in methyl and ethyl alcohol, acetic acid, ethyl acetate and hot chloroform, sparingly soluble in hot benzene and insoluble in petrol. It crystallised in plates from benzene and in needles from dilute alcohol m.p. 193-194°. The product crystallised from benzene contained considerable quantity of benzene (0.8 mol of benzene was retained by 1 mol of acid). The substance crystallised from dilute alcohol was analysed. (Found: C, 71.9 ; H, 5.8 per cent. Eq. wt., 142.9. $C_{17} H_{16} O_4$ requires C, 71.8 ; H, 5.6 per cent. Cq. wt., 142.) Barium and calcium salts were soluble while silver lead, copper and zinc salts were insoluble in water. Silver salt was analysed. (Found : Ag in silver salt, 42.9 per cent. $C_{17} H_{14} O_4 Ag_2$ requires Ag, 43.4 per cent.)

α α *Diphenyl glutaric anhyaride.*—It was prepared by heating the acid with acetic anhydride on water bath for half an hour. It was soluble in chloroform, ethyl acetate, benzene and insoluble in petrol. It crystallised in blades from chloroform petrol mixture m.p. 142-143°. (Found : C, 76.5 ; H, 5.3 per cent. $C_{17} H_{14} O_3$ requires C, 76.7 ; H, 5.3 per cent.)

Monoanilide of α α *diphenyl glutaric acid:*—It was prepared by heating the anhydride with the requisite quantity of aniline in benzene solution for ten minutes on water bath. It was soluble in methyl and ethyl alcohol, ethyl acetate but insoluble in chloroform, petrol and benzene. It crystallised from alcohol in short stout needles, m.p. 208°. (Found : Eq. wt. 353.8. $C_{23} H_{21} O_3$ N requires Eq. wt., 359.0.)

Mono p toluidide of α α *diphenyl glutaric acid :*—It was prepared in a similar manner. It was soluble in all the common solvents except petrol. It crystallised in leaves from benzene petrol mixture, m.p. 168°. (Found : Eq. wt., 375.2. $C_{24} H_{23} O_3$ N requires Eq. wt., 373.)

——*Diphenyl glutarimide :*—It was prepared by heating the anhydride at 180-190° in a current of dry ammonia. It was soluble in common solvents and crystallised in plates from alcohol mp.p 158°-159°. (Found : N, 5.0 per cent. $C_{17} H_{15} O_2 N$ requires N, 5.2 per cent.)

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CONDENSATION OF O-METHOXY PHENYL SUCCINIC ANHYDRIDE WITH o-AND m-CRESOL METHYL ETHERS

By

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THE condensation of o-methoxy phenyl succinic anhydride by Friedel and Craft's reaction with some phenol methyl ethers was described in a previous paper where it was mentioned that in case of o-and m-cresol methyl ethers both types of keto acids were obtained (Jour. Bom. Univ. 1940, Vol. IX Part 3, page 150). The constitutions of these keto acids have now been determined and a number of their derivatives have been prepared for their characterisation.

The condensation of o-methoxy phenyl succinic anhydride with o-cresol methyl ether gave two products which were separated by hot alcohol. The one which was less soluble, on further purification had m.p. 183°, and the other had m.p. 140-141°. Analytical results showed that both had the formula $C_{19} H_{20} O_5$. That the point of attachment of o-methoxy phenyl succinic acid residue to the o-cresol methyl ether was the same in both, viz., it was para to the methoxy group was proved in the following manner. The grignard reagent prepared from 2 methoxy 5 bromo toluene was boiled with o-methoxy phenyl succinic anhydride in benzene solution when the same acids were isolated from the reaction product. Attempt to synthesise one of them by the addition of potassium cyanide and subsequent hydrolysis to 2-4' dimethoxy 3' methyl chalcone according to the method of Hahn and Lapworth (J.C.S. 1904, 1358) was unsuccessful. The acid m.p. 183°, however, reacted with salicylaldehyde in presence of dry hydrogen chloride to give deep red pyrillium derivative and with piperonal in presence of sodium ethoxide to give a gummy piperonylidene derivative. Hence its constitution was ∝-o methoxy phenyl-β-4-methoxy 3-toluoyl propionic acid. The acid m.p. 140° on the other hand did not give these derivatives hence its constitution was β-o-methoxy phenyl β-4-methoxy 3-toluoyl propionic acid.

The condensation of o-methoxy phenyl succinic anhydride with m-cresol methyl ether gave two keto acids which were separated by acetic acid, and had m.p. 152° and 126°. The same two keto-acids were obtained by the action of o-methoxy phenyl succinic anhydride on the grignard reagent prepared from 6-bromo 3-methoxy-toluene. The acid m.p. 152° was synthesised by Hahn and Lapworth's method (loc.

cit.) 2-methyl-4 methoxy-acetophenone, (Dalal, Bokil and Nargund, Jour. Bom. Univ. 1939, Vol. VIII, Part 3, page 195), when condensed with o-methoxy-benzaldehyde gave 4′-2-dimethoxy 6′ methyl-chalcone. Addition of potassium cyanide to this chalcone and the hydrolysis of the resulting product gave a keto-acid m.p. 152°, identical with the one obtained in the condensation. The acid m.p. 152° also gave a pyrillium derivative hence its constitution was ∝ -o-methoxy-phenyl β-4-methoxy-2-toluoyl-propionic acid. The acid m.p. 126° was therefore β-o-methoxy phenyl β-4-methoxy-2-toluoyl-propionic acid.

<div align="center">EXPERIMENTAL</div>

The yields of the condensation products using the conditions and the mode of working described by Dalal, Bokil and Nargund (*loc. cit.*) are given in the following table.

Phenol ether used	Total yields in different solvents	Products obtained
o-cresol methyl ether	93 per cent in nitrobenzene	(1) 44 per cent of ∝ -o-methoxy phenyl β-4-methoxy 3-toluoyl-propionic acid (2) 49 per cent of β-o-methoxy-phenyl--β-4-methoxy-3-toluoyl-propionic acid
	96 per cent in acetylene tetrachloride	54 per cent of (1) 42 per cent of (2)
m-cresol methyl ether	80 per cent in nitrobenzene	(3) 60 per cent of ∝ -o-methoxy phenyl β-4-methoxy 2-toluoyl propionic acid (4) 20 per cent of β-o-methoxy-phenyl-β-4-methoxy 2 toluoyl propionic acid
	85 per cent in acetylene tetrachloride	58 per cent of (3) 27 per cent of (4)

Separation of the two keto acids from the condensation product from o-cresolomethylether :—The crude product on dissolving in boiling alcohol and cooling gave pure ∝ -o-methoxy phenyl β-4-methoxy 3-toluoyl propionic acid. The mother liquor on concentration gave the other product.

∝ -*o-methoxy phenyl β-4-methoxy 3-toluoyl propionic acid:*—It was soluble in acetic acid, chloroform, ethyl acetate, hot benzene and hot alcohol but insoluble in petrol and water. It crystallised in needles from alcohol or dilute acetic acid. m.p. 183°. (Found : C, 69.4 ; H, 6.3, per cent. Eq. wt., 331.0; Ag in silver salt, 25.1 per cent. $C_{19} H_{20} O_5$ requires C, 59.5 ; H, 6.1 per cent. Eq. wt, 328.0. $C_{19} H_{19} O_5$ Ag requires Ag 24.8 per cent.) The pyrylium derivative of the above was obtained when its solution in methyl alcohol was saturated in cold with dry hydrogen chloride. It was deep red, insoluble in the common solvents but soluble in sodium hydroxide solution. It did not melt up to 300°.

The piperonylidene derivative was a gummy mass which could not be crystallised.

Methyl ∝ *-o-methoxy phenyl* β-*4-methoxy 3-toluoyl propionate* prepared by the silver salt method was soluble in benzene, ether, alcohol and chloroform but insoluble in petrol. It crystallised from ether petrol in thin needles m.p. 101°. (Found : C, 69.9 ; H, 6.5 per cent. $C_{20} H_{22} O_5$ requires C, 70.2 ; H, 6.4 per cent.)

Ethyl ∝ *-o-methoxyphenyl* β-*4-methoxy 3-toluoyl propionate* prepared similarly, crystallised from ethyl acetate in plates m.p. 63-65°. |(Found: C, 70.5 , H, 6.7 per cent. $C_{21} H_{24} O_5$ requires C, 70.8 ; H, 6.7 per cent.)

β-*o-methoxy phenyl* β-*4-methoxy 2-toluoyl propionic acid :*—It was soluble in acetic acid, ethyl acetate, chloroform and insoluble in petrol. It crystallised from dilute alcohol in plates m.p. 140-141°. (Found: C, 69.6; H, 6.3 per cent. Eq. wt, 327.3. $C_{19} H_{20} O_5$ requires C, 69.5 ; H, 6.1 per cent. Eq. wt., 328.) The above acid did not give pyryllium and piperonylidene derivatives. The semicarbazone of the above acid crystallised from alcohol in granules m.p. 200°. (Found : N, 11.6 per cent. $C_{20} H_{23} O_5 N_3$ requires N, 10.9 per cent.)

Methyl β-*o-methoxy phenyl* β-*4-methoxy 2-toluoyl propionate* prepared by the silver salt method, crystallised from alcohol in rectangular plates m.p. 113°. (Found : C, 70.2 ; H, 6.5 per cent. $C_{20} H_{22} O_5$ requires C, 70.2 ; H, 6.4 per cent.)

Ethyl β-*o-methoxy phenyl* β-*4-methoxy 2-toluoyl propionate* prepared similarly, crystallised from boiling alcohol in rhombic plates m.p. 93°. (Found : C, 70.7; H, 6.9 per cent. $C_{21} H_{24} O_5$ requires C, 70.8; H, 6.7 per cent.)

2-4'-dimethoxy 3'-methyl chalcone :—A solution of 3-methyl 4-methoxy acetophenone (4 gms.), (Dalal, Bokil and Nargund, *loc. cit.*), alcohol, (10 c.c.) and o-methoxy benzaldehyde (4 gms.) was warmed on water bath and a solution of 50 per cent. sodium hydroxide (8 gms.) was gradually added. It was heated for ten minutes and left overnight. It was soluble in all the common solvents except petrol. It crystallised from dilute acetic acid in reddish yellow prisms m.p. 79°. (Found : C, 76.4 ; H, 6.5 per cent. $C_{18} H_{18} O_3$ requires C, 76.6 ; H, 6.4 per cent.) The chalcone did not react with potassium cyanide under any conditions nor did it give a crystalline bromine addition product.

Separation of the two keto acids from condensation product from m-cresol methyl ether :—The product was dissolved in hot acetic acid and left over several days when one substance gradually crystallised in granules. Dilution of the mother-liquor with water gave the other product. Both were purified by recrystallisation.

∝ *-o-methoxy phenyl* β-*4-methoxy 2-toluoyl propionic acid:*—It was soluble in benzene, chloroform, alcohol, ethyl acetate and hot acetic acid but insoluble in petrol. It crystallised in needles from acetic acid. m. p. 151-152°. (Found: C, 69.7 ; H, 6.1 per cent. Eq. wt., 330.0. $C_{19} H_{20} O_5$ requires C, 69.5 ; H, 6.1 per cent. Eq. wt., 328.)

Synthesis of the above acid :—*4'-2-dimethoxy 6-methyl chalcone :*—It was obtained as a gummy yellowish mass when 4-methoxy 6-methyl acetophe

none and o-methoxy benzaldehyde were allowed to react in presence of 50 per cent. sodium hydroxide solution. It was purified by distillation under reduced pressure; b.p. at 11 mm. was 210-215°. (Found: C, 76.0; H. 6.1 per cent. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.1 per cent.) It reacted with potassium cyaniade under the conditions of Hahn and Lapworth (*loc. cit.*) On hydrolysis and purification a keto acid was obtained m.p. 150° which did not depress the m.p. of the acid m.p. 152° described above.

Methyl α *-o-methoxy phenyl* β-4-*methoxy* 2-*toluoyl propionate* :—It was soluble in the common solvents and crystallised from alcohol in needles. m.p. 115°. (Found: C, 70.1 ; H, 6.2 per cent. $C_{20}H_{22}O_5$ requires C, 70.2 ; H, 6.4 per cent.)

Ethyl α *-o-methoxy phenyl* β-4-*methoxy* 2-*toluoyl propionate* crystallised from alcohol in needles m.p. 122°. (Found: C, 70.6 ; H, 6.9 per cent. $C_{21}H_{24}O_5$ requires C, 70.8 ; H, 6.7 per cent.)

β-*o-methoxy phenyl* β-4-*methoxy* 2-*toluoyl propionic acid* :—It was soluble in benzene, chloroform, alcohol, ethyl acetate and hot acetic acid but insoluble in petrol. It crystallised from dilute acetic acid in granules m.p. 125°. (Found: C, 69.2 ; H, 6.5 per cent. Eq. wt., 327.7. $C_{19}H_{20}O_5$ requires C, 69.5 ; H, 6.1 per cent. Eq. wt., 328.) The methyl and ethyl esters of the above acid were gummy masses which could not be purified by any means.

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ALKYL SUCCINIC ACIDS, PART I-n-TET-RADECYL AND n-HEXADECYL SUCCINIC ACIDS

By

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A LKYL succinic acids are required in this laboratory in connection with the work on synthetical anthelmintics. Alkyl succinic acids with alkyl groups up to hexyl are already known. Of the higher alkyl succinic acids the only compound reported in literature is tetradecyl succinic acid of which only the anhydride is known. (B. *23*, 2358, Bid. Zeit. *22*, 419-432.) We have now prepared tetradecyl succinic acid by a different method and characterised it by a number of derivatives. We have also prepared hexadecyl succinic acid an account of which appears below.

The most convenient mode of preparation of n-alkyl-succinic acids was to start with easily available n-fatty acids. These were then brominated by Hell Volhard method followed by treatment with absolute alcohol when ∝ bromo esters were obtained in good yields. Condensation of these bromo esters with ethyl malonate in presence of sodium ethoxide gave tricarboxylic esters. Boiling these esters with concentrated hydrochloric acid did not bring about the expected hydrolysis and decarboxylation. Hence these were hydrolysed by alkali to the corresponding tricarboxylic acids which were then decarboxylated by heating above their melting points. The final yields of the succinic acids were about sixty per cent.

The m.p. of tetradecyl succinic acid found by us was 110°, while that reported in literature is 121. The anhydride of the acid, had the same m.p., *viz.*, 74° as reported in literature. (The m.p. 89 given for this anhydride in Beilstein is a misprint.)

Tetradecyl succinic acid formed a sparingly soluble sodium salt the exact solubility of which is being determined to see whether it could be used to detect sodium ions analytically.

EXPERIMENTAL

The compounds are described in tabular form for the sake of brevity

Name of the Compound	Formula	Properties	Analysis Found	Analysis Required for
n-Hexadecane 1-1-2-tricarboxylic acid.	$C_{19}H_{34}H_6$	Crystallised in granules from acetic acid m.p. 135°. Ba, Ca, Pb and Ag salts were insoluble in water	C, 63.4; H, 9.6; Eq. wt., 119.7	C, 63.7; H, 9.5; Eq. wt., 119.3
n-Tetradecyl succinic acid	$C_{18}H_{34}O_4$	Crystallised in leaves from acetic acid m.p. 110°	C, 68.9; H, 11.0; Eq. wt., 155.2	C, 68.8; H, 10.8; Eq. wt., 157.0
Dimethyl n-tetradecyl succinate	$C_{20}H_{38}O_4$	Colourless liquid b.p. 220° at 20 mm. $N_D^{27.50} = 1.4440$ $D_4^{27.5} = 0.9180$	C, 69.9; H, 11.4	C, 70.2; H, 11.1
Diethyl n-tetradecyl succinate	$C_{22}H_{42}O_4$	Colourless liquid b.p. 230° at 20 mm. $N_D^{27.5} = 1.4430$ $D_4^{27.5} = 0.9058$	C, 71.3; H, 11.5	C, 71.3; H, 11.3
n-Tetradecyl succinic anhydride	$C_{18}H_{32}O_3$	Thin wooly needles from benzene petrol mixture m.p. 74.	C, 73.2; H, 10.9	C, 73.0; H, 10.8
n-Tetradecyl succinimide	$C_{18}H_{33}O_2N$	Flat needles from ethyl alcohol m.p. 98-99°	N, 5.5 per cent. Eq. wt., 386.2	N, 4.9 per cent. Eq. wt., 389.0
Monoanilide of tetradecyl succinic acid.	$C_{24}H_{39}O_3N$	Short needles from alcohol m.p. 124-125°		
Mono p-toluidide of tetradecyl succinic acid	$C_{25}H_{41}O_3N$	Needles from alcohol m.p 118-120°	Eq. wt., 409.0	Eq. wt., 403.0
n-Octadecane 1-1-2-tricarboxylic acid.	$C_{21}H_{38}O_6$	Needles or granules from methyl alcohol m.p. 135°; Ba, Ca, Pb and Ag salts were insoluble.	C, 65.5; H, 10.1; Eq. wt., 127.2	C, 65.3; H, 9.8; Eq. wt., 128.6
n-Hexadecyl succinic acid	$C_{20}H_{38}O_4$	Needles from acetic acid m.p. 89-90°	C, 69.9; H, 11.1; Eq. wt., 172.0	C, 70.2; H, 11.1; Eq. wt., 171
Dimethyl n-hexadecyl succinate	$C_{22}H_{42}O_4$	Colourless liquid b.p. 205-210° at 10 mm, $N_D^{28.5} = 1.4460$ $D_4^{28.5} = 0.9264$	C, 71.5; H, 11.5	C, 71.3; H, 11.3
Diethyl n-hexadecyl succinate	$C_{24}H_{46}O_4$	Liquid b.p. 215-220 at 10 mm. $N_D^{28.5} = 1.4435$ $D_4^{28.5} = 0.9108$	C, 72.5; H, 11.3	C, 72.4; H, 11.5
a-Hexadecyl succinic anhydride	$C_{20}H_{36}O_3$	Plates from petrol benzene mixture or by cooling benzene solution m.p. 63°	C, 74.3; H, 11.3	C, 74.1; H, 11.1
n-Hexadecyl succinimide	$C_{20}H_{37}O_2N$	Granules from alcohol m.p 94.95°	N, 4.7 per cent	N, 4.3

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PECHMANN CONDENSATION OF PHENOLS WITH ETHYL-Y-PHENYL ACETOACETATE

By

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THE Pechmann condensation of β-ketonic esters with phenols has-been extensively studied in recent years. Various ∝ -substituted aceto-acetic esters have been condensed with phenols and phenolic com-pounds but no systematic attempt has however been made so far to study the reactivity of γ-substituted acetoacetic esters in the Pechmann reaction. The reactivity of ethyl-γ-phenyl acetoacetate which was prepared by the method of Sonn and Litten (Ber., 1933, 66 B, 1512) has now been studied.

It has been found that ethyl-γ-phenyl acetoacetate condenses with re-sorcinol, orcinol, pyrogallol, phloroglucinol and ∝ -naphthol to give 4-benzyl coumarins. Resorcinol and phloroglucinol were condensed with ethyl-γ-phenyl acetoacetate in presence of sulphuric acid by Sonn and Litten (loc. cit.) and our results agree with theirs. The coumarin structure of the compounds was proved by the preparation of the cinnamic acid derivatives.

Phenol, β-naphthol, quinol, m-cresol, methyl-β-resorcylate and res-acetophenone did not condense with ethyl-γ-phenyl acetoacetate either in presence of sulphuric acid or in presence of phosphoryl chloride, phos-phorus pentoxide and anhydrous aluminium chloride.

The results show that a γ-phenyl substituent in ethyl acetoacetate has considerable inhibiting effect on the course of the Pechmann reaction, for, phenol, m-cresol, quinol and methyl-β-resorcylate which do not condense with ethyl-γ-phenyl acetoacetate do condense with ethyl ace-toacetate to give coumarins in presence of H_2SO_4, as found by previous workers. (Pechmann and Duisberg, Ber., 1883, 16, 2119, Fries and Klostermann, ibid., 1906, 39, 871, Borsche, ibid., 1907, 40, 2732, Shah et al., J. Indian Chem. Soc., 1937, 14, 717.)

Whether the phenyl group in the γ-position has greater inhibiting effect on the course of Pechmann condensation than a phenyl group in the ∝ -position or not cannot be stated as some of the above phenols, methyl-β-resorcylate and resacetophenone do not seem to have been condensed with ethyl- ∝ -phenyl acetoacetate.

The presence of the phenyl group in the γ-position has a greater retarding effect on the course of the Pechmann condensation than the presence of a negative group like the carbethoxy, for, ethyl acetone

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dicarboxylate which may be taken as ethyl γ-carbethoxy acetoacetate has been found to condense with m-cresol and quinol by Dey (J.C.S., 1914, 1606) and with methyl-β-resorcylate by Sethna and Shah (J. Ind. Chem. Soc., 1940, *17*, 37).

EXPERIMENTAL

7-Hydroxy-4-benzyl coumarin :—To a mixture of ethyl-γ-phenyl aceto-acetate (3 g.) and resorcinol (1.6 g.), concentrated sulphuric acid (15 c.c.) was slowly added. The reaction mixture was allowed to stand over-night and then poured in powdered ice. The product obtained was crystallised from methyl alcohol in needles, m.p. 214-215°. Sonn and Litten (*loc. cit.*) give the same m.p.

It is soluble in alcohol, insoluble in ether and water and it gives blue fluorescence with alkali.

The acetyl derivative :—7-Hydroxy-4-benzyl-coumarin (0.5 g.) was refluxed on a wire gauze for 3 hours with anhydrous sodium acetate (1.4 g.) and acetic anhydride (5 c.c.). The product obtained on adding the reaction mixture to water was crystallised from rectified spirit in needles, m.p. 138-139°. (Found : C, 73.4, H, 4.8 ; C_{18} H_{14} O_4 requires C, 73.5, H, 4.8 per cent.)

The benzoyl derivative :—7-Hydroxy-4-benzyl-coumarin (0.5 g.) was dissolved in sufficient quantity of pyridine and heated on a boiling water bath for two hours with benzoyl chloride (2 c.c.). The reaction mixture was added to dilute H_2SO_4, when a pasty mass was obtained which solidified on keeping in a frigidiare. The product obtained was washed with sodium bicarbonate solution to remove benzoic acid and crystallised from alcohol in fine silky needles, m.p. 180-181°. (Found : C, 77.6, H, 4.5 ; C_{23} H_{16} O_4 requires C, 77.5, H, 4.5 per cent.)

The methyl ether :—7-Hydroxy-4-benzyl-coumarin (0.5 g.) dissolved in acetone (50 c.c.) was refluxed for 20 hours with fused K_2 CO_3 (1.g.) and methyl iodide (5 c.c.). The acetone was removed by evaporation and water was added. The product obtained was crystallised from very dilute alcohol in tiny shining needles, m.p. 140-141°. (Found : C, 76.7, H, 5.3 ; C_{17} H_{14} O_3 requires C, 76.7, H,5.3 per cent.)

2 : 4-Dimethyl-β-benzyl cinnamic acid :—7-Hydroxy-4-benzylcoumarin (1.g.) was dissolved in acetone, dimethyl sulphate (8 c.c.) was added and the reaction mixture heated on a boiling water bath for about 5 to 8 minutes. Sodium hydroxide (5% 30 c.c.) was then added gradually with constant shaking. The heating being carried on all the time. More dimethyl sulphate (10 c.c.) and sodium hydroxide (40 c.c.) were added alternately with shaking. Finally, excess of sodium hydroxide was added and heating continued for about half an hour. It was then left overnight. Next day the solution was filtered and acidified with Conc. HCl. It was then kept in the frigidiare and on the next day the solid obtained was filtered, washed and treated with sodium bicarbonate solution. The product obtained on the acidification of the sodium

bicarbonate solution was crystallised from dilute alcohol in tiny shining needles, m.p. 130°. It decolourises bromine water and dilute potassium permanganate solution. It dissolves in sodium bicarbonate solution with effervescence. (Found : C, 72.7, H, 6.4 ; $C_{18} H_{18} O_4$ requires C, 72.5, H, 6.4 per cent.)

5-Hydroxy-4-benzyl-7-methyl coumarin :—Prepared from orcinol (1.1 g.), ethyl-γ-phenyl acetoacetate (2 g.) and sulphuric acid (80%; 15 c.c.) as usual, was crystallised from alcohol in fine needles, m.p. 248-249°. It gave deep yellow colouration with sodium hydroxide. (Found : C, 76.7, H, 5.3 ; $C_{17} H_{14} O_3$ requires C, 76.7, H, 5.2 per cent.)

The acetyl derivative :—Prepared as before, was crystallised from rectified spirit in tiny needles, m.p. 139-140°. (Found : C, 74.1, H, 5.4 ; $C_{19} H_{16} O_4$ requires C, 74.0 ; H, 5.3 per cent.)

The methyl ether :—Prepared as before, was crystallised from very dilute alcohol in tiny shining needles, m.p. 140-141°. (Found : C, 76.7, H, 5.7 ; $C_{18} H_{16} O_3$ requires C, 77.1, H, 5.8 per cent.)

2 : 6-Dimethoxy-4-methyl-β-benzyl cinnamic acid :—Prepared as before, was crystallised from water with a few drops of alcohol in tiny shining silky needles, m.p. 153-154°. (Found : C, 72.8, H, 6.4 ; $C_{19} H_{20} O_4$ requires C, 73.1, H, 6.4 per cent.)

7 : 8-Dihydroxy-4-benzyl coumarin :—Prepared from pyrogallol (1.6 g.), ethyl-γ-phenyl acetoacetate (2 g.) and sulphuric acid (80%; 15 c.c.) as before was crystallised from alcohol after keeping the condensation products in a frigidiare for a couple of days in needles, m.p. 192-194°. (Found : C, 71.6, H, 4.7 ; $C_{16} H_{12} O_4$ requires C, 71.6, H, 4.5 per cent.)

The acetyl derivative :—Prepared as before, was crystallised from rectified spirit in needles, m.p. 168°. (Found : C, 68.3, H, 4.7 ; $C_{20} H_{16} O_6$ requires C, 68.1, H, 4.5 per cent.)

The methyl ether :—Prepared as before, was crystallised from dilute alcohol in needles, m.p. 178-180°. (Found : C, 72.5, H, 5.7 ; $C_{18} H_{16} O_4$ requires C, 72.9, H, 5.6 per cent.)

5 : 7-Dihydroxy-4-benzyl coumarin :—Prepared from phloroglucinol (1.6 g.), ethyl-γ-phenyl acetoacetate (2.0 g.) and sulphuric acid (80% ; 15 c.c.) as before, was crystallised from alcohol (charcoal) after keeping the products in a frigidiare for a couple of days in fine shining needles, m.p. 274-276°. Sonn and Litten (*loc. cit.*) give m.p. 260° (Decomp.). (Found : C, 71.6, H, 4.7, $C_{16} H_{12} O_4$ requires C, 71.6, H, 4.5 per cent.)

The acetyl derivative :—Prepared as usual, was crystallised from rectified spirit in tiny needles, m.p. 152-154°. (Found : C, 68.4, H, 4.6 ; $C_{20} H_{16} O_6$ requires C, 68.2, H, 4.6 per cent.)

The methyl ether :—Prepared as usual, was crystallised from dilute alcohol in needles, m.p. 182-185°. (Found : C, 72.8, H, 5.7 ; C_{18} H_{18} O_4 requires C, 72.9, H, 5.5 per cent.)

2 : 4 6-Trimethoxy-γ-benzyl coumarin :—Prepared as before, was crystallised from water with a few drops of alcohol in fine silky needles, m.p. 144-146°. (Found : C, 70.0, H, 6.1 ; C_{19} H_{20} O_5 requires C, 69.6, H, 6.1 per cent.)

α -Naphtha-4-benzyl coumarin :—prepared from α -naphthol (1.4 g.) and ethyl-γ-phenyl acetoacetate (2 g.) and sulphuric acid (80% ; 15 c.c.) as before, was crystallised from alcohol (charcoal) in needles, m.p. 174°. (Found : C, 83.9, H, 5.2 ; C_{20} H_{14} O_2 requires C, 83.9, H, 4.9 per cent.)

Attempts to prepare the cinnamic acid derivative from this product by the usual method were unsuccessful.

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DISSOCIATION CONSTANTS OF β-SUBSTITUTED PHENYL GLUTARIC ACIDS—PART I

By

N. L. PHALNIKAR AND B. V. BHIDE

THORPE, Ingold and collaborators have shown in a series of papers (J. 1915, 1080 ; ibid 1921, 305, 951 ; ibid 1928, 1594, 2267 ; ibid 1929, 691 ; ibid 1931, 2253) that the tetrahedral valency angle of a carbon atom is changed by the attachment of different heavy groups to the carbon atom or by the inclusion of the same in a ring system. This is known as the *Valency—Deflexion Hypothesis.*

Ingold and Gane (J. 1928, 1594, 2270) have determined the dissociation constants of substituted malonic and glutaric acids and have calculated the distances between the two carboxyl groups of these acids using Bjerrum's equation (Z. Physikal Chem. 1923, *106*, 219). These distances have been shown to be in agreement with the valency deflexion hypothesis.

The study of the effects of the substituents on the valency angle has been restricted to groups like H, H ; Me, H ; Et, H ; Me, Me ; Et, Et; cyclopentane, cyclohexane, etc. The effect of the phenyl groups on the valency angle has not been studied. This is partly due to the fact that many phenyl substituted glutaric acids were not known, and those, which were known, failed to undergo the reaction by which other acids were studied (*cf.* Thorpe & Haeridi, J. 1925, 1237).

The dissociation constants of the following acids have been determined in the present investigation :—

(1) glutaric acid,

(2) β—phenyl glutaric acid,

(3) β—phenyl β—methyl glutaric acid, and

(4) ββ—diphenyl glutaric acid.

The determinations of dissociation constants of dibasic acids have been made by following the pH value of the solution of the acid as it is being neutralised by alkali (*cf.* Auerbach and Smolezyk, Z. Physikal Chem., 1924, *110*, 83 ; Britton, J. 1925, 1896 ; Gane & Ingold, J. 1928, 1594 and 2271 et. sec. Burton, Hamer and Acree, Jour. Bureau of Standards

1936, *16*, 575 and Abichandani & Kulkarni-Jatkar, J. Ind. Inst. Sci.
1938, Part 3,7417). Ingold and Gane (loc. cit.) have followed the
method of Auerbach and Smolczyk (loc. cit.) for calculation. However,
Britton (loc. cit.) has pointed out that the equation used by Auerbach and
Smolczyk is based on several approximations. The dissociation constants
are, therefore, likely to be inaccurate. In our calculation we have fol-
lowed the method of Burton, Hamer and Acree.

<div align="center">EXPERIMENTAL</div>

Preparation of material :—

β *phenyl glutaric* was obtained by the hydrolysis of ethyl β phenyl pro-
pane— ᾳ ᾳ ɣ tricarboxylate with hydrochloric acid (Michael, J. Pr. 2,
35, 352). ββ *Diphenyl glutaric* acid and β—*Phenyl—β—methyl glutaric cacid*
were prepared according to the method described by Nargund and
Phalnikar (J. Univ. Bom. 1937, Vol. VI, Part II, 102 and ibid 1936,
Vol. V, part II, 105).

Purification of Acids :—

The acids were dissolved in an equivalent quantity of sodium carbonate
and the sodium salts of the acids were obtained by evaporation to dryness
on a water bath. They were then washed with acetone and ether. The
washed sodium salts were dissolved in water and acidified. The acids
obtained on acidification were crystallised from water twice or thrice.

Solutions of Acids and Alkali :—

The solutions of acids were made by taking a weighed quantity of acid
and dissolving in a known volume of conductivity water. All solutions
were prepared in conductivity water and were stored either in pyrex
bottles or in bottles coated inside with paraffin wax.

Standard sodium hydroxide solution was prepared from carbonate
free sodium hydroxide prepared by the action of water on sodium.

Determination of Dissociation Constants :—

The potentiometric titrations of the acids were carried out at 25°c and
the dissociation constants were calculated from the pH values of the
solutions at each addition of the alkali.

The pH measurements, made with a glass electrode and a saturated
calomel electrode were read directly on a pH Colemann electrometer
(Model 3). The electrometer was standardised using a standard sodium
acetate, acetic acid buffer. To test the accuracy of the measurements,
pH value of glutaric acid solution E—(0.002763 M) was determined. It
was found to be 3.23. Ingold and Gane (loc. cit.) give the pH value of
the same solution as 3.24. This shows that the apparatus gave sufficiently
accurate values.

Calculation of the dissociation constants:—

Using the method of Burton, Hamer and Acree (loc. cit.), we have cal-
culated out the dissociation constants of the acids. The relevant data
is given in tables I and II for each acid.

K_1^c and K_2^c, the first and second dissociation constants (classical) have been calculated on the assumption that the two carboxyl groups do not titrate simultaneously. These values are given in table II for each acid. The large variations in the values of K_1^c and K_2^c show that the two carboxylic groups titrate simultaneously almost throughout the whole range. In order to allow for the simultaneous titration of the two carboxyl groups we have used the following equation given by Burton, Hamer and Acree :

$$C_{An} = \frac{M_{H2An} \times K_1^c \times K_2^c}{(C_H)^2 + C_H \times K_1^c + K_1^c K_2^c}$$

Where C_{An} = ionic concentration of the di salt

$M_{H2}{}^{An}$ = stoichiometrical concentration of the acid

C_H = ionic concentration of the hydrogen ion

K_1^c = first dissociation constant (classical)

K_2^c = second   ,,   ,,   ,,

We calculated at each stage the values of C_{An}, C_{HAn} (*ionic* concentration of H_{An} ion) and C_{H2An} (ionic concentration of H^2An) by assuming suitable values for K_1^c and K_2^c. We have calculated K_1^c and K_2^c by the method of successive approximations. The new values of K_1^c and K_2^c are given in table III for each acid and are fairly constant.

Burton, Hamer and Acree (loc. cit) have shown that the liquid junction potential between the saturated potassium chloride bridge and the titrating solution is sufficiently high (Circa, 26 milli-volts). In the case of the acids used by us the relevant data required for such a calculation were not available. Hence this potential has been neglected.

The thermodynamic dissociating constants also have been calculated by the following formulae (*cf.* Burton, Hamer & Acree, loc. cit.) :

$$\text{Log } K_1^a = \text{Log } K_1^c - \text{Log } f_h - \frac{A\sqrt{\mu}}{1+\sqrt{\mu}}$$

$$\text{Log } K_2^a = \text{Log } K_2^c - \text{Log } f_h - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} + A\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$$

where A = 0.506 and μ, is the ionic strength.

In our calculation we have taken log f_h to be zero as the solutions are very dilute. The values of K_1^c and K_2^c for all acids are summarised in table No. 1.

The value of K_1^a for glutaric acid has been found to be 5.89×10^{-5} while earlier workers give 4.6×10^{-5} (*cf.* Ingold & Gane, Vogel J. 1935, 21). This difference can be shown to be entirely due to the method of calculation and measurement. We have recalculated the dissociation constant for glutaric acid using Gane and Ingold's data (page 152).

It will be seen that if K_1^c is assumed to be 4.6×10^{-5}, the values of K_1^c recalculated (after allowing for simultaneous titration) are about 6.4, which is the value obtained by us. When K_1^c is assumed to be 6.27×10^{-5} the recalculated values are fairly constant. On examining the values of dissociation constants of malonic acid by various workers, it has been shown by Burton, Hamer and Acree, that such large differences are observed.

In the following tables the following symbols, not already mentioned, have been used.

J = Equivalent concentration of Na salts

$M_{H2An} = U$ = Stoichiometrical concentration of the un-neutralised acid

M_{NaHAn} = ,, ,, of sodium acid salt

M_{Na2An} = ,, ,, of disodium salt of the acid

C_{NaHAn} = ionic concentration of the mono sodium salt

GLUTARIC ACID

TABLE I

Stoichiometrical concentrations in the titrations of 200 ccs. of 0.00527 M acid by 0.0764 N Sodium hydroxide

ccs. of 0.0764 N NaOH	J=Equiv. Conc. of Na Salts $\times 10^4$	$MH_2An \times 10^4$	MH_2An =$U \times 10^4$	$MNaHAn \times 10^4$	$MNa_2An \times 10^4$
0.0	0.0 cc	52.7	52.74	0.0	
2.0	7.565	52.18	44.615	7.565	
4.1	15.35	51.65	36.3	15.35	
6.0	22.86	51.15	28.29	22.86	
8.0	29.38	50. 7	21.32	29.38	
10.0	36.39	50.15	13.76	36.39	
11.0	39.83	49.94	10.11	39.83	
12.0	43.25	49.72	6.47	43.25	
13.0	46.62	49.48	2.86	46.62	
14.0	49.98	49.24		48 50	0.74
15.0	53.31	49.02		44.73	4.82
21.0	72.59	47.695		22.800	24.895
22.0	75.70	47.475		19.250	28.225
23.0	78.79	47.22		15.65	31.57
23.5	80.34	47.16		13.98	33.18
24.0	81.87	47.06		12.25	34.81
25.0	84.87	46.89		8.01	37.98
26.0	84.87	46.89		5.38	41.26
27.0	91.20	46.415		1.630	44.785

GLUTARIC ACID

TABLE II

Data for Titration

ccs. of 0.0764 N NaOH	pH	$CH \times 10^n$	n	$K_1^c \times 10^5$	$K_2^c \times 10^6$
0.0	3.1	7.943	4	....	....
2.0	3.55	2.818	4	6.995	
4.1	3.87	1.349	4	6.446	
6.0	4.09	8.128	5	7.00	
8.0	4.25	5.623	5	8.11	
10.0	4.42	3.802	5	10.46	
11.0	4.51	3.090	5	12.66	
12.0	4.6	2.512	5	17.6	
13.0	4.69	2.042	5		
14.0	4.75	1.778	5		
15.0	4.82	1.514	5		
21.0	5.35	4.467	6		5.20
22.0	5.45	3.546	6		5:31
23.0	5.58	2.630	6		5.44
23.5	5.64	2.291	6		5.05
24.0	5.75	1.778	6		5.43
25.0	5.89	1.288	6		5.49
26.0	6.11	7.762	7		5.95
27.0	6.70	1.995	7		5.48

GLUTARIC ACID

TABLE III

Dissociation Constants

ccs. of NaOH	$CNa_2An \times 10^4$	$CNaHAn \times 10^4$	$CH_2An \times 10^4$	$K_1^c \times 10^5$	$K_2^c \times 10^6$
4.1	0.633	15.433	35.57	6.33	5.11
6.0	1.39	20.89	28.87	6.11	5.20
8.0	2.362	25.218	23.12	6.27	5.15
10.0	3.95	28.97	17.23	6.48	5.11
11.0	5.07	30.00	14.87	6.30	5.18
12.0	6.426	30.648	12.65	6.13	5.22
			Mean	6.27	5.153

Dissociation Constant of glutaric acid calculated from Ingold's data

Assuming $K_1 = 4.6 \times 10^{-5}$ and

$K_2 = 5.34 \times 10^{-6}$

(Values of K_1 and K_2 calculated by Ingold)

ccs. of NaOH	$CNa_2An \times 10^4$	$CNa\,HAn \times 10^4$	$CH_2An \times 10^4$	$K_1^c \times 10^5$	$K_2^c \times 10^6$
5.2	3.07	30.875	20.95	6.8	4.44
3.99	1.688	25.689	28.27	6.39	4.39
2.81	0.837	20.043	35.52	6.34	4.23
1.59	0.298	12.967	43.895	6.64	4.48

Dissociation Constant

calculated by assuming $K_1 = 6.27 \times 10^{-5}$ and

$K_2 = 5.15 \times 10^{-6}$ calculated by us

1.59	0.365	12.835	43.96	6.57	4.82
2.81	0.99	19.737	35.67	6.22	5.07
3.99	1.93	25.21	28.51	6.22	5.1
5.2	3.38	30.255	21.265	6.57	5.01
			Mean	6.47	5.00

β PHENYL GLUTARIC ACID

TABLE I

Stoichiometrical concentrations in the titration of 100 ccs. of 0.007253 M acid by 0.07640 N Sodium hydroxide

ccs. of NaOH	J = Equiv. Conc. of Na Salts × 10⁴	$MH_2An \times 10^4$	$MH_2An = U \times 10^4$	$MNaHAn \times 10^4$	$MNa_2An \times 10^4$
0.0	0.00	72.53	72.53		
2.0	14.98	71.1	56.12	14.98	
3.0	22.25	70.47	48.17	22.25	
4.1	30.09	69.7	39.69	30.00	
5.0	36.68	69.08	33.70	36.38	
6.0	43.24	68.41	25.17	43.24	
7.0	49.98	67.8	17.82	49.98	
9.5	66.27	66.20		66.13	0.07
10.0	69.45	65.93		62.41	3.52
13.0	87.80	64.2		40.51	23.69
14.0	93.82	63.61		33.40	30.21
15.0	99.65	63.07		26.49	36.58
16.0	105.38	62.51		19.64	42.87
17.2	112.12	61.87		11.62	50.25
19.0	121.93	60.95			61.03

β Phenyl Glutaric Acid

Table II

Data for Titration

ccs. of NaOH	pH	CH 10^n	n	$K_1^c \times 10^5$	$K_2^c \times 10^6$
0.0	3.15	7.08	4		
2.0	3.62	2.399	4	7.94	
3.0	3.8	1.585	4	8.11	
4.1	3.98	1.047	4	8.58	
5.0	4.1	7.944	5	8.97	
6.0	4.22	6.025	5	10.75	
7.0	4.33	4.677	5	13.35	
2.5	4.6	2.512	5		
10.0	4.68	2.09	5		
13.0	5.05	8.99	6		5.21
14.0	5.2	6.31	6		5.72
15.0	5.35	4.467	6		6.08
16.0	5.54	2.884	6		6.3
17.2	5.85	1.413	6		6.1
19.0	9.65				

β Phenyl Glutaric Acid

Table III

Dissociation Constants

ccs. of NaOH	CNa_2 An $\times 10^4$	CNaHAn $\times 10^4$	CH_2An $\times 10^4$	K_1^c $\times 10^5$	K_2^c $\times 10^6$
2.0	0.442	16.495	54.6	8.31	5.6
3.0	0.884	22.068	47.52	7.88	5.92
4.0	1.69	28.96	39.05	8.04	5.89
5.0	2.523	32.128	34.43	7.6	6.09
6.0	3.68	36.48	28.25	7.91	5.98
7.0	5.08	40.29	22.43	8.5	5.83
			Mean	8.04	5.88

β Phenyl β Methyl Glutaric Acid

Table I

Stoichiometrical concentrations in the titration of 100 ccs. of 0.008213 M acid by 0.07640 N Sodium hydroxide

ccs. of NaOH	J = Equiv. Conc. of Na Salts ×10⁴	MHAn × 10⁴	MH₂An × 10⁴ =U	MNaHAn ×10⁴	MNa₂An ×10⁴
0.0	0.0	82.13	82.13		
1.0	7.565	81.3	73.73	7.565	
2.6	19.36	80.1	60.74	19.36	
4.0	29.24	79.0	49.6	29.24	
5.0	36.38	78.2	41.82	36.38	
6.0	43.24	77.5	34.26	43.24	
7.0	49.98	76.65	26.67	49.98	
10.0	69.45	74.66	5.21	69.45	
10.7	73.9	74.2			
11.0	75.71	74.0		72.29	1.71
12.0	81.85	73.3		64.78	8.55
15.0	99.65	71.4		43.15	28.25
16.0	105.38	70.80		36.22	34.58
17.0	111.0	70.20		29.40	40.80
18.0	116.54	69.6		22.66	46.94
19.0	121.98	69.04		16.10	52.94
20.0	127.9	68.43		9.96	58.47

β Phenyl β Methyl Glutaric Acid

Table II

Data for Titration

ccs. of NaOH	pH	CH 10ⁿ	n	$K_1^c \times 10^5$	$K_2^c \times 10^5$
0.0	3.22	6.025	4		
1.0	3.41	3.89	4	6.4	
2.6	3.65	2.239	4	8.08	
4.0	3.84	1.445	4	9.26	
5.0	3.94	1.148	4	10.6	
6.0	4.05	8.901	5	11.55	
7.0	4.15	7.08	5		
10.0	4.40	3.98	5		
10.7	4.49	3.236	5		
11.0	4.52	3.02	5		
12.0	4.6	2.512	5		
15.0	4.84	1.445	5		0.946
16.0	5.0	1.0	5		0.956
17.0	5.13	7.414	6		1.03
18.0	5.25	5.624	6		1.165
19.0	5.45	3.548	6		1.167
20.0	5.72	1.906	6		1.12
21.6	9.05				

β PHENYL β METHYL GLUTARIC ACID

TABLE III

Dissociation Constants

ccs. of NaOH	CNa An × 10⁴	CNaHAn × 10	CH₂ An × 10⁴	K_1^C × 10⁵	K_2^C × 10⁵
1.0	0.3543	10.746	70.2	8.11	0.941
2.0	0.923	19.75	59.43	8.33	0.94
4.0	1.878	27.089	50.043	8.24	0.95
5.0	2.659	32.21	43.33	8.84	0.915
6.0	3.834	36.46	37.21	8.96	0.915
			Mean	8.49	0.93

ββ DIPHENYL GLUTARIC ACID

TABLE I

Stoichiometrical concentrations in titrations of 200 ccs. of 0.001314 M acid by 0.03755 N Sodium hydroxide

ccs. of NaOH	J = Equiv. Conc. of Na salts × 10	MHAn × 10⁵	MH An × 10⁴ = U	MNaHAn × 10⁴	MNa An × 10₄
0.0	0.0	13.14	13.14		
0.5	0.937	13.11	12.173	0.937	
1.0	1.868	13.08	11.212	1.868	
1.5	2.796	13.04	10.244	2.796	
3.0	5.55	12.94	7.39	5.55	
4.0	7.36	12.88	5.52	7.36	
7.0	12.70	12.70	0.00	12.70	
8.0	14.44	12.63		10.82	1.81
10.0	17.88	12.51		7.14	5.37
11.0	19.57	12.45		5.33	7.12
12.0	21.26	12.4		3.54	8.86
13.0	22.92	12.34		1.76	10.58
13.4	23.58	12.31		1.04	11.27
13.8	24.23	12.29		0.35	11.94
14.0	24.56	12.28		0.00	12.28

$\beta\beta$ Diphenyl Glutaric Acid

TABLE II

Data for Titration

ccs. of NaOH	pH	CH 10^n	n	$K_1^c \times 10$	$K_2^c \times 10^5$
0.0	3.8	1.585	4		
0.5	3.85	1.416	4	3.09	
1.0	3.91	1.23	4	3.82	
1.5	3.98	1.047	4	4.37	
3.0	4.18	6.60	5	6.1	
4.0	4.29	5.13	5	8.06	
7.0	4.62	2.398	5		
8.0	4.73	1.78	5		
10.0	5.00	1.0	5		0.752
11.0	5.18	6.606	6		0.883
12.0	5.4	3.98	6		0.996
13.0	5.7	1.995	6		1.2
13.4	5.9	1.26	6		1.36
13.8	6.28	5.25	7		1.79
14.0	6.5	3.16	7		

$\beta\ \beta$ Diphenyl Glutaric Acid

TABLE III

Dissociation Constants

ccs. of NaOH	CNa$_2$An $\times 10^4$	CNaHAn $\times 10^4$	CH$_2$An $\times 10^4$	$K_1^c \times 10^5$	$K_2^c \times 10^5$
0.5	0.2616	1.831	11.017	4.16	1.14
1.0	0.333	2.432	10.315	4.37	1.12
1.5	0.434	2.975	9.631	4.37	1.13
3.0	0.887	4.4366	7.616	4.42	1.153
4.0	1.311	5.25	6.318	4.58	1.14
			Mean	4.38	1.136

TABLE No. 1

Dissociation Constants (classical) of Acids

Acid	K_1^c	K_2^c
Glutaric acid	6.27×10^{-5}	5.153×10^{-6}
β phenyl glutaric acid	8.04×10^{-5}	5.88×10^{-6}
β phenyl β methyl glutaric acid	8.49×10^{-5}	9.3×10^{-6}
$\beta\ \beta$ diphenyl glutaric accid	4.38×10^{-5}	1.136×10^{-5}

DISCUSSION

The following table summarises the results obtained :—

TABLE No. 2

Thermodynamic Dissociation Constants of Acids

Acid	$K_1{}^a$	$K_2{}^a$	'r' * A.U.
Glutaric acid	5.88×10^{-5}	4.26×10^{-6}	5.74
β phenyl glutaric acid	7.53×10^{-5}	4.84×10^{-6}	5.23
β methyl glutaric acid**	5.77×10^{-5}	6.28×10^{-7}	2.27
β phenyl β methyl glutaric acid	8.00×10^{-5}	7.78×10^{-6}	7.52
β β dimethyl glutaric acid**	2.03×10^{-4}	5.51×10^{-7}	1.57
β β diphenyl glutaric acid	4.27×10^{-5}	1.053×10^{-5}	38.8

* 'r' is the distance between the two carboxyl groups calculated according to Bjerrum's equation :—

$$\text{Log } K_1{}^a - \text{Log } K_2{}^a - 0.6 = \frac{3.1 \times 10^{-8}}{r}$$

** These values are taken from Gane and Ingold's paper (J. 1028, 2268).

It will be seen from the above table that as the phenyl group is introduced in the β position the first and second dissociation constants are both affected and the ratio of $K_1{}^a$ to $K_2{}^a$ becomes smaller as the number of phenyl groups in the β position is increased.

Ingold and collaborators (loc. cit.) have determined the dissociation constants of β alkyl substituted glutaric acids and have shown that as the β substituent becomes more bulky the ratio of $K_1{}^a$ to $K_2{}^a$ increases, with a corresponding decrease in the value of 'r', and a decrease in the valency angle.

Similarly, if a phenyl group is considered as a bulky group, its effect should be to decrease the value of 'r' and the ratio of $K_1{}^a$ to $K_2{}^a$ should increase. This is true in the case of β phenyl glutaric acid as the value of 'r' in this acid is less than that in glutaric acid. This observation is in agreement with the fact that β phenyl glutaric acid forms an anhydride. But, contrary to expectation, the value of 'r' in this acid is greater than that in β methyl glutaric acid.

It is also expected that the effect of the substituents should be enhanced in the case of β β diphenyl glutaric acid. However, the observed dissociation constants of this acid and of β phenyl β methyl glutaric acid show a decrease in the ratio of $K_1{}^a$ to $K_2{}^a$ and an increase in the value of 'r'. This observation is also in agreement with the fact that β diphenyl glutaric acid does not form an anhydride (cf. Nargund and 'halnikar, loc. cit.).

The observed distance 'r' in case of glutaric acid is 9.2 A.U.   This value is in agreement with that expected on the assumption that glutaric acid has a straight chain (Zig-Zag) configuration, (cf. Ingold and Gane, loc. cit.) and very different from the value given in Table No. 2. These facts evidently point out that (1) Bjerrum's equation is not applicable and (2) the effect of a phenyl group is not only due to its bulky nature but is also due to its inductive effects.

Ingold and Gane state that in the β alkyl substituted glutaric acids chosen by them for comparison the internally propagated polar factors would be negligible and therefore the value of 'r' would be good enough for comparison, though not physically accurate. Obviously in the phenyl substituted glutaric acids studied in this investigation the effect of the internally propagated field must be operating and cannot be neglected. The work of Dippy and collaborators (J. C. S. 1937, 1008 ; ibid 1934, 1888), on the dissociation constants of phenyl substituted mono-basic acids, has shown that a phenyl group has an appreciable effect on the dissociation constants of the acids due to its inductive effect (—I) and that this effect can be transmitted along a saturated carbon chain as far as the third carbon atom.   In light of these observations it is clear that in the phenyl substituted glutaric acids studied by us the effect of a phenyl group will not be only due to its bulky nature but will also be due to its —I effect which may even predominate and thus Bjerrum's equation will be inapplicable in case of these acids and the value of 'r' calculated from it will have no significance.

Further work is in progress.

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REACTION VELOCITY IN HETERO-GENEOUS LIQUID-LIQUID SYSTEMS

By

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H ETEROGENEOUS reactions in the widest sense of the term, constitute a class of reactions, important both from the theoretical and the industrial points of view. Almost all catalytic reactions, reactions in which colloids take part, a large number of enzymatic reactions and also other physiological processes are examples of heterogeneous reactions. Theoretically the following types of heterogeneous reactions are possible :

(1) Solid-solid, (2) solid-liquid, (3) liquid-liquid, (4) liquid-gas and (5) solid-gas. In the present article the heterogeneous reactions between two liquids which are immiscible with each other have been mainly discussed.

If any two phases which react with each other are brought in contact, then the reaction velocity will depend upon two factors :

(1)   The actual velocity of the chemical process, which depends upon such factors as concentration, pressure, temperature, etc.

(2)   The velocity with which the products of reaction are removed from the interface and that with which fresh reactants are brought to the interface from the interior of the phases. The latter depends upon the velocity of diffusion of the products and of the reactants.

The net velocity of the heterogeneous reaction will be the resultant of the speeds of the chemical and the diffusion processes and like the consecutive reactions in homogeneous systems, it will be determined by the slowest reaction. Thus two types of heterogeneous reactions are possible :

(1)   those in which the speed of the chemical change taking place at the interface is faster than the speed of diffusion,

and (2) those in which the speed of the diffusion process is faster than that of the chemical change.

It is thus evident that diffusion processes play a very important part in the consideration of heterogeneous reactions.

The laws of diffusion of gases have been formulated by Graham and further modified by workers like Carlson (Medd. Vet-Akad. Nobel Inst. 2, No. 5, 1911), Kuenen (Kuenen-Ostwald-Drucker—Handbuch der allgem. Chemie, Leipzig, 1919, pp. 1-139) and Stefan (Wiener Sitz. Ber. 65, 323, 1872). The diffusion of liquids or of dissolved substances into liquids is governed by Fick's law which is mathematically represented as

$$dS = -Dq \frac{dc}{dx} dt. \dots\dots\dots\dots\dots (1)$$

where dS is the quantity of a substance diffusing through a cross-section q in the time interval dt, dc/dx is the concentration gradient, and D is a constant depending on the nature of the substance and is termed the diffusion coefficient. The force determining the diffusion is the same as that which causes osmotic pressure.

If the dissolved substance is a salt, which is capable of dissociating into ions, the problem becomes more complex. While to a certain extent ions are free to diffuse independently of each other, the electrostatic attraction between oppositely charged ions will not allow any very great separation of the positively and negatively charged ions. Taking into account the driving force causing the diffusion and the electrostatic force between the ions, Nernst arrived at the following expression :

$$dS = -\frac{2 \ UV}{U+V} \ RT \ . \ q \frac{dc}{dx} dt. \ \dots\dots\dots\dots (2)$$

where U and V are the ionic mobilities of the kation and the anion, respectively, R the gas constant, T the absolute temperature and other terms have the same significance as in equation (1).

If we compare the expressions (1) and (2), we find that

$$D = \frac{2UV}{U+V} \ RT. \ \dots\dots\dots\dots\dots (3)$$

Various authors have studied the diffusion velocities of dissociated salts and have obtained values which agree very well with those calculated according to the Nernst formula.

An important point in connection with the diffusion of dissolved substances is the temperature effect on the diffusion velocity. In general, the velocity of diffusion increases by a rise in tempreature. Öholm (Zeit. physik. Chem., 50, 309, 1904 ; 70, 378, 1910 ; Medd. Vet-Akad. Nobel Inst., 2, Nos. 23, 24, 26, 1912) has shown that the temperature coefficient also depends upon the value of the diffusion coefficient D in the above equation. The following table compiled by him gives an idea of the magnitude of these two factors :

TABLE I

D	2.4	2.0-1.8	1.6-1.4	1.2-1.1	0.8 0.7	0.4-0.3
∝	0.018	0.020	0.022	0.025	0.029	0.035

The values of α, the temperature coefficient, have been calculated from the following equation, employing the measured values of the diffusion coefficients D_2 and D_1 at temperatures T_2 and T_1, respectively:

$$\frac{D_2}{D_1} = 1 + \alpha \ (T_2 - T_1) \ldots \ldots \ldots (4)$$

In the study of reaction velocities, temperature coefficients are generally calculated for a rise of 10° in temperature. Also it is well known that temperature coefficients lying between 2 to 4 are commonly observed for chemical processes in homogeneous systems. If Öholm's results in Table I are worked out for 10° rise in temperature, an average value of about 1.28 corresponding to $\alpha = 0.025$, is obtained for the temperature coefficient. This value of the temperature coefficient is much less than the value (2 to 4) usually obtained for chemical reactions in the homogeneous system.

The temperature coefficient can thus be employed to determine the nature of the slow process taking place in a heterogeneous reaction. If it is found to be very much lower than 2, then it is a reaction in which diffusion processes are slower than the chemical reactions and consequently determine the net velocity. If, on the other hand, it is higher than 2, then the chemical reaction is slower than the diffusion process and determines the net velocity.

A general theory of the kinetics of heterogeneous reactions has been put forward by Nernst on the basis of the results obtained by Noyes and Whitney (Zeit. physik. Chem., *23*, 689, 1897) on the dissolution of a solid substance in the form of a cylinder when it is rotated at a uniform speed in a solvent. It has been postulated by Noyes and Whitney that in the process of solution a layer of a saturated solution of the solid is formed at the surface of the solid cylinder and that as the solute diffuses into the remainder of the liquid, the strength of the saturated solution is maintained at a constant level by more and more of the solid going into solution. If S is the concentration of the saturated layer, x that of the bulk of the solution at a time t, the rate of dissolution is given by

$$\frac{dx}{dt} = C \ (s-x) \quad \ldots \ldots \ldots \ldots \ldots (5)$$

where C is a constant. This is a direct consequence of Fick's law, since the amount diffusing is proportional to the concentration gradient. This equation is identical in form with the velocity equation for unimolecular reactions. This cannot however be taken as a direct proof of the unimolecular nature of the solution process, because it is based on the assumption that only the rate of diffusion determines the net reaction velocity.

Nernst's general theory involves two main assumptions : (*i*) a very rapid reaction at the interface and (*ii*) a comparatively slow diffusion process of the resultants and reactants. A number of reactions between solutions of iodine in aqueous potassium iodide and various metals studied by Van Name and co-workers (Z. physik. Chem., *73*, 97, 1910; Am. J. Sci., *32*, 207, 1911 ; *36*, 543, 1913) have been found to be in accordance with this theory. However, it has been shown that these

assumptions are not at all valid for all types of heterogeneous reactions. There are certain chemical reactions in which the velocity of the chemical change is slower than the diffusion process and in these cases the net velocity is determined by the rate of the chemical reaction and not by that of the diffusion process.

· The application of these fundamental ideas have been extended to the velocity of heterogeneous liquid-liquid reactions. Systematic studies of such reactions are few, although the chemist is daily using these reactions in the laboratory and the factory. Extractions with ether and benzene from aqueous solutions, saponification of liquid oils by aqueous alkali, nitrations and sulphonations of liquid organic compounds by nitric and sulphuric acids are but a few of the reactions, the velocity of which is of great practical importance in the efficient carrying out of large and small scale processes.

On considering the matter in detail, it will be found that there are very few pairs of liquids which are entirely insoluble in each other. On this account in most heterogeneous liquid-liquid reactions a small amount of homogeneous reaction is generally taking place simultaneously with the heterogeneous reaction. Thus in the study of the kinetics of the reaction between carbon disulphide and aqueous alkali Karve and Dole (J. Ind. Chem. Soc., *12*, 719, 1935) found that owing to the appreciable solubility of carbon disulphide in the aqueous layer, the total reaction is the sum of two factors, the homogeneous reaction in the alkali phase and the heterogeneous reaction at the interface.

This reaction has been thoroughly investigated by Karve and Dole and the effects of various factors such as the speed of shaking, concentration of the alkali and that of the solvent for CS_2, wherever used, temperature, total quantity of the reactants, the addition of neutral electrolytes, etc., on the velocity of reaction have been examined. For this purpose the reactants were shaken together in glass stoppered bottles on a shaking machine kept in a large air thermostat regulated by a toluene bulb thermo-regulator. The speed of shaking was maintained constant by regulating the motor and the revolutions were measured either by a tachometer or by means of a stroboscopic disc attached to the shaft of the motor. After the reaction was completed, the amount of the reaction was determined by estimating the amount of sulphur in the aqueous layer as barium sulphate.

It has been found that the velocity of the reaction increases with the speed of shaking although no direct proportionality exists between the two. It is further found that there is a limit to the increase in the reaction velocity, which could not be exceeded even with very high shaking speeds. This is probably due to the centrifugal effects on the heavier of the two liquids, so that very high velocities of shaking do not produce proportionately greater or more intimate mixing of the two phases.

The increase in the velocity of the reaction is found to be directly proportional to the concentration of the alkali. When solvents were used for the carbon disulphide, besides the concentration of that reagent, the velocity is also found to depend on the nature of the solvent. Other factors being the same, the velocity is largest in xylene and decreases,

n order, is monochlorobenzene, petroleum ether, toluene and mono-i brombenzene. No single property like the dielectric constant, viscosity density, etc., of the solvent used, seems to explain this particular order and the effect appears to be due to the combined action of one or more of their properties.

The reaction has another peculiarity which was noticed by Karve and Dole for the first time. It has already been mentioned that carbon disulphide is appreciably soluble in the aqueous phase. (0.1634 g. dissolve in 100 c.c. of water at 26°. cf. Rex, Compt. rend., 99, 892, 1884 ; 100, 773, 1885). The solubility decreases to a certain extent in solutions of other salts, but is even then quite appreciable. It is 0.1334 in 0.5 N, 0.1115 in 1 N and 0.0832 in 2 N NaCl. It is evident, therefore, that the heterogeneous reaction will always be accompanied by a homogeneous reaction taking place in the aqueous phase. In fact, by comparing the reaction between a saturated aqueous solution of carbon disulphide and alkali with the heterogeneous reaction, it was ascertained that the homogeneous reaction forms the major part of the total reaction.

It was found, that owing to the high vapour pressure of carbon disulphide at the ordinary temperature, the empty space above the liquid mixture very soon becomes saturated with the vapour of that substance, and a reaction also takes place between carbon disulphide vapour and aqueous alkali at the gas-liquid interface. As long as a sufficient quantity of carbon disulphide is present in the reaction vessel, this would naturally be a constant factor, as the diminution of the concentration of the alkali during the course of the reaction would be the only factor affecting it.

It has been stated above that the net reaction velocity of a heterogeneous reaction depends upon the speed of the chemical process and the speed of diffusion. Shaking, stirring or other forms of agitation would be expected to affect only the second process. Now, just as the products of the reaction are removed from the interface by diffusion, it is also possible to remove them by chemical action with another chemical substance. In the case of the reaction between carbon disulphide and alkali it could be achieved by the addition of hydrogen peroxide to the reaction mixture. The product of the reaction of alkali with carbon disulphide is a complex mixture of various salts of the acids of sulphur, chiefly the thionates, sulphite and thiosulphate. All these are easily oxidised by hydrogen peroxide at the ordinary temperature and hence the presence of this substance would tend to reduce the concentration of the products of the reaction near the interface. The effect would therefore be the same as an increase in the velocity of diffusion and would result in an increase in the net reaction velocity. Expectations in this respect were fully corroborated and it was also seen that the increase is approximately proportional to the concentration of the hydrogen peroxide added.

For the study of the effect of the addition of a neutral salt like sodium chloride, two different factors have to be considered. It has already been mentioned, that the addition of a neutral salt reduces the solubility of carbon disulphide in the alkali layer. This would cause a diminution in the homogeneous reaction in the alkali phase. Further, the addition of a neutral salt would lower the dissociation of the alkali and

thus would bring about a decrease in the heterogeneous reaction at the liquid-liquid interface. In the experiments conducted by Karve and Dole the second effect was found to be very small, as fairly high concentrations of the alkali were used.

The effect of the increase in the total quantity of carbon disulphide (in the absence of a solvent) was seen to be very small, the reason being that the major part of the total reaction is the homogeneous reaction taking place in the alkali phase, and a very small part is a heterogeneous reaction. Naturally, therefore, the aqueous phase becomes saturated with carbon disulphide even when small quantities of it are present and an increase in the total quantity of carbon disulphide cannot have any effect on the homogeneous reaction. A very slight increase in the velocity of the heterogeneous reaction was the only effect observed.

The reaction between carbon disulphide and alkali is thus a typical homo-heterogeneous reaction in which the reaction at the gas-liquid interface introduces some complication.

A purely heterogeneous reaction, in which the homogeneous part is absent, takes place between benzoyl chloride and water (Karve and Dole, J. Ind. Chem. Soc., *12*, 733, 1935) since benzoyl chloride is practically insoluble in water. The reaction thus takes place only at the interface between the two substances. The products of the reaction diffuse into the interior and the reactants diffuse towards the interface. A product of the reaction is benzoic acid whose solubility in water is very limited and in order to prevent the formation of a third solid phase, it was necessary to use some solvent which would be immiscible with water and would dissolve both the benzoyl chloride and the benzoic acid.

In the study of this reaction also it has been found that the reaction velocity increases with increase in (1) shaking, (2) the concentration of the benzoyl chloride and (3) the temperature. The effect of an increase in the speed of shaking is found to be greater in this reaction than in the reaction between carbon disulphide and alkali ; since only heterogeneous reaction is taking place in this case, it is also the one that is affected by agitation. Further it has been found that the nature of the solvent has some effect on the velocity of the reaction and the decreasing order of their efficiency is carbon tetrachloride, xylene, carbon disulphide, monochlorobenzene, monobrombenzene and chloroform. As one of the reactants was always present in excess in these experiments, the reaction velocity has been found to agree with the unimolecular equation within the limits of experimental error. However, there was observed a small but gradual rise in the values of the unimolecular constant, which fact was later found to be of some significance.

Karve and Dole (J. Univ. Bom., *7*, Part III) also noticed the gradual rise in the value of K in the reaction between a large number of other acid chlorides like cinnamoyl chloride, phthalyl chloride, o-, m-, and p-chlorbenzoyl chloride, p-brombenzoyl chloride, o-iodobenzoyl chloride, o-, m-, and p-nitrobenzoyl chloride, dinitrobenzoyl chloride, p-methoxybenzoyl chloride and water. They assigned this rise to the following four factors : (i) the formation of hydrochloric acid in gradually increasing quantities which has an increasing catalytic effect on the

velocity of the reaction ; this was proved by the addition of known quantities of sulphuric acid to the reaction mixture which increased the velocity of the reaction to a considerable extent; (*ii*) a similar but very small effect is also caused by the organic acid liberated ; (*iii*) there is a slight, but distinct rise in temperature due to the collision of the droplets of the non-aqueous phase with the aqueous phase and to the heat of the reaction; and (*iv*) the inertia of the process of splitting up of the phases into droplets, so that the extent of the interface, which is small at the beginning, gradually increases as the shaking goes on and brings about an increase in the reaction velocity. The effect of the last factor was easily seen by noting the time taken by several reaction mixtures, which had been shaken for different lengths of time, to separate completely into two layers. Mixtures which had been shaken only for a short time, had large sized droplets and separated out very quickly, while those which had been shaken for a longer time took longer to separate out. Further the effect of the inertia was eliminated completely when the vessels were given a preliminary vigorous shaking by hand before being fixed on the shaking machine, since fine droplets were obtained right from the beginning.

In order to throw further light on the relative velocities of the chemical reaction and the diffusion process a number of temperature coefficients were determined. The temperature coefficient for the reaction between benzoyl chloride and water was found to be 1.57, that for the reaction between phthalyl chloride and water was 1.85, and that for the reaction between m-nitrobenzoyl chloride and water was 2.54. It would appear, therefore, that in the case of benzoyl and phthalyl chlorides the diffusion process, being the slower of the two, determines the net velocity, while with m-nitrobenzoyl chloride the chemical reaction is the slower and is the determining factor.

Some reactions involving the hydrolysis of benzyl, butyl and isoamy acetates, were then taken up for study (*cf.* Karve and Mehendale, J. Univ. Bom., *8*, Part III). These reactions have a peculiar feature which was not noticed in any of the reactions mentioned before. This refers to the solubility of the alcohols, produced by hydrolysis, in the aqueous phase. In the case of benzyl acetate both the ester and the benzyl alcohol are insoluble in water, but butyl and iso-amyl alcohols are appreciably soluble in water and they in their turn dissolve some of the ester. Thus in the case of butyl and iso-amyl acetates the reaction is purely heterogeneous at the start but later becomes homo-heterogeneous. The values of K calculated according to the monomolecular formula were found to increase much more rapidly in the case of these two esters than with benzyl acetate. The temperature coefficients of these reactions were found to be between 2.4 and 3, indicating that the chemical process determines the net velocity.

The results obtained by Karve and co-workers point out that the diffusion-layer theory of Noyes-Whitney-Nernst (Zeit. physik. Chem., *23*, 689, 1897 ; *47*, 52, 1904) which postulates a saturated layer at the interface, where the chemical reaction is supposed to take place at a fairly rapid rate, and assumes that the net velocity of the reaction depends mainly on the speed of the diffusion, can only be considered

to be a first attempt towards a satisfactory explanation. There is no valid ground for supposing that a saturated layer is present at the interface or that the chemical reaction is always very rapid as compared with the diffusion process. Further, this theory cannot explain the dependence of the velocity of the reaction on other factors besides the velocity of diffusion.

Another theory based on the formation of an adsorption layer at the interface has been suggested. According to this theory a layer of adsorbed molecules of one reactant is formed on the surface of the other reactant and the chemical reaction takes place at this adsorbed layer. This theory is probably more applicable to reactions taking place on the surface of catalysts. However, in liquid-liquid heterogeneous reactions this theory alone cannot explain all the observed results. For instance, if the two layers are agitated separately, keeping the extent of the surface of contact constant, there should be no increase in the velocity of the reaction, since the agitation cannot affect the adsorption layer. However, an increase in the velocity has actually been observed under these circumstances. It appears that the diffusion of the products away from the interface and the diffusion of the reactants to the interface are of great importance, for these will be the only factors affected under the experimental conditions described above.

When two liquids are agitated by shaking or stirring, the phases are split up into droplets. It appears that each droplet behaves as a separate entity on the surface of which the reaction takes place probably through the formation of an adsorbed layer. A layer of the products of the reaction is thus formed on the surface of the droplets and the velocity of the diffusion of these products into the interior must be a determining factor. The results of investigations obtained so far lead to the conclusion that neither the chemical nor the diffusion process is the *sole* determining factor of the velocity of heterogeneous reactions. The adsorption layer is certainly present and can explain the mechanism of the chemical process, but the diffusion process has been proved to be of equal importance.

SCIENCE NOTES

On the Electromagnetic Theories of the Scattered Light

By

M. M. PARANJPE

A THEORY of the scattered light based on the electromagnetic theory of light was first given by Love[1]. Rayleigh[2] applied a correction to the theory given by Love and obtained expressions for the amplitude of the scattered light by spherical particles of any size, in terms of the size of the particles and the wavelength of the incident light.

In 1908 Mie[3] developed a different method of solving the problem and obtained different expressions for the intensity of the scattered light in terms of the particle-size and the incident wavelength.

It can be shown that the theoretical values obtained for the intensity of the scattered light by Love and Rayleigh are identical with the values obtained by Mie.

On the electromagnetic theory of the scattered light given by Mie

$$I_1 = \frac{\lambda^2}{4\pi r^2} \left| \sum_{n=1}^{\infty} \left\{ A_n \pi_n + P_n[\pi_n \mu - \pi'_n(1-\mu^2)] \right\} \right|^2$$

$$I_2 = \frac{\lambda^2}{4\pi r^2} \left| \sum_{n=1}^{\infty} \left\{ A_n[\pi_n \mu - \pi'_n(1-\mu^2)] + P_n \pi_n \right\} \right|^2$$

where I_1 and I_2 are the intensities of the scattered light polarised in vertical and horizontal planes respectively. 'λ' is the wavelength of the incident light 'r' is the distance of the observer from the spherical particles and 'n' is the serial number of the partial waves and can have any integral value from 1 to ∞.

$$A_n = \frac{(-1)^n(2n+1)}{n(n+1)} \left\{ \frac{\beta\, S'_n(\alpha)S_n(\beta)}{[\beta\, S_n(\beta)C'_n(\alpha) - \alpha S'_n(\beta)C_n(\alpha)]} \frac{-\alpha S_n(\alpha)S'_n(\beta)}{-i[\beta\, S'_n(\alpha)S_n(\beta) - \alpha\, S_n(\alpha)S'_n(\beta)]} \right\}$$

$$P_n = \frac{(-1)^{n+1}(2n+1)}{n(n+1)} \left\{ \frac{\beta\, S_n(\alpha)S'_n(\beta)}{[\beta\, S'_n(\beta)C_n(\alpha) - \alpha S_n(\beta)C'_n(\alpha)]} \frac{-\alpha S'_n(\alpha)S_n(\beta)}{-i[\beta S_n(\alpha)S'_n(\beta) - \alpha S'_n(\alpha)S_n(\beta)]} \right\}$$

where $\alpha = \dfrac{2\pi\rho}{\lambda}$ 'ρ' is the radius of the spherical particle. $\beta = m'\alpha$ where 'm'' is the refractive index of the material of the spherical particle with respect to the surrounding medium.

$$S_n(x) \;=\; x^{n+1}\left(-\frac{1}{x}\frac{d}{dx}\right)^{n}\frac{\sin x}{x}$$

$$C_n(x) \;=\; x^{n+1}\left(-\frac{1}{x}\frac{d}{dx}\right)^{n}\frac{\cos x}{x}$$

$$S'_n(x) \;=\; \frac{d}{dx}\,S_n(x)$$

$$C'_n(x) \;=\; \frac{d}{dx}\,C_n(x)$$

$$\pi_n \;=\; \pi_n(\mu) \;=\; \frac{\partial}{\partial\mu}\left[\,P_n(\mu)\,\right]$$

where 'P_n' is called the Legendre's function of 'μ'.
$\mu = \cos\theta$ where 'θ' is the angle between the direction of the incident light and the direction in which the intensity of the scattered light is to be evaluated.

——3——

On the Love-Rayleigh theory of the scattered light

$$Y = \sum_{h=1}^{\infty}(-1)^{n+1}\frac{(2n+1)}{n\,(n+1)}\left[M_n\left\{\mu P'_n - n(n+1)P_n\right\}+N_n\,P'_n\right]\frac{e^{ik(ct-r)}}{kr}$$

$$\frac{xZ - zX}{r} = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{(2n+1)}{n(n+1)}\left[N_n\left\{\mu P'_n - n(n+1)P_n\right\}+M_nP'_n\right]\frac{e^{ik(ct-r)}}{kr}$$

where $/Y/$ and $\dfrac{/xZ - zX/}{r}$ are amplitudes of the scattered light polarised in vertical and horizontal planes respectively.

$$k = \frac{2\pi}{\lambda} \qquad kr = \frac{2\pi r}{\lambda}$$

$$P'_n = \frac{\delta}{\delta\mu}\,(P_n) \;=\; \pi_n \quad \text{in Mie's theory.}$$

P_n is the Legendre's fuction of $\mu = \cos\theta$.

$$N_n = \frac{K\,\psi_{n-1}(\eta) - \left\{(K-1)\dfrac{n}{2n+1} + \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\right\}\psi_n(\eta)}{-K\,E_{n-1}(\eta) + \left\{(K-1)\dfrac{n}{2n+1} + \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\right\}E_n(\eta)}$$

$$M_n = \frac{\psi_{n-1}(\eta) - \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\,\psi_n(\eta)}{-E_{n-1}(\eta) + \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\,E_n(\eta)}$$

'K' is the dielectric constant of the material of the spherical particle with respect to the surrounding medium.

'M_n' is obtained from N_n by replacing 'K' by the magnetic permeability μ of the material of the particle with respect to the surrounding medium, which may be supposed to be equal to one.

$\eta = kp = \dfrac{2\pi p}{\lambda}$ where p is the radius of the particle and λ is the wavelength of the incident light.

Hence $\eta = \alpha$ in Mie's theory.

$\eta' = m'\eta = \beta$ in Mie's Theory.

$$\psi_n(x) = (-1)^n . 1\cdot 3 \ldots (2n+1)\left\{\frac{1}{x}\frac{d}{dx}\right\}^n \frac{\mathrm{Sin}\,x}{x}$$

$$= \frac{1.3\ldots(2n+1)}{x^{n+1}}\,S_n(x)$$

$$E_n(x) = \bar\psi_n(x) - i\,\bar\psi_n(x)\cdot$$

where $\bar\psi_n(x) = (-1)^n 1\cdot 3 \ldots (2n+1)\left\{\frac{1}{x}\frac{d}{dx}\right\}^n \frac{\cos x}{x}$

$$= \frac{1.3\ldots(2n+1)}{x^{n+1}}\,C_n(x)$$

———4———

Consider N_n. The numerator of N_n is equal to

$$K\,\psi_{n-1}(\eta) - \left\{(k-1)\frac{n}{2n+1} + \frac{\psi_{n-1}(\eta)'}{\psi_n(\eta')}\right\}\psi_n(\eta)$$

$$= KS_{n-1}(\alpha)\frac{1\cdot 3\ldots(2n-1)}{\alpha^n} - \left\{(k-1)\frac{n}{2n+1} + \frac{S_{n-1}(\beta)}{S_n(\beta)}\cdot\frac{\beta}{2n+1}\right\}$$

$$\frac{S_n(\alpha).1.3\ldots(2n+1)}{\alpha^{n+1}}.$$

$$= \frac{1}{S_n(\beta)}\cdot\frac{1\cdot 3\ldots(2n-1)}{\alpha^n}\left\{K\,S_{n-1}(\alpha)\,S_n(\beta) - \frac{n}{\alpha}K\cdot S_n(\beta)\right.$$

$$\left. S_n(\alpha) + \frac{n}{\alpha}S_n(\alpha)\,S_n(\beta) - S_{n-1}(\beta)\,S_n(\alpha)\frac{\beta}{\alpha}\right\}$$

$\therefore \quad K = m'^2 = \beta^2/\alpha^2$

$\therefore$ The numerator of N_n

$$= \frac{1}{S_n(\beta)} \cdot \frac{1.3\ldots(2n-1)}{\alpha^n} \cdot \frac{\beta}{\alpha^2} \left\{ \beta\, S_n(\beta)\left[S_{n-1}(\alpha) - \frac{n}{\alpha}S_n(\alpha)\right] \right.$$

$$\left. + \alpha\, S_n(\alpha)\left[\frac{n}{\beta}S_n(\beta) - S_{n-1}(\beta)\right]\right\}$$

$\therefore S'_n(x) = S_{n-1}(x) - \frac{n}{x}S_n(x)$

$\therefore$ The numerator of N_n

$$= \frac{1}{S_n(\beta)} \cdot \frac{1.3\ldots(2n-1)}{\alpha^n}\frac{\beta}{\alpha^2}\left\{\beta S_n(\beta)S'_n(\alpha) - \alpha S_n(\alpha)S'_n(\beta)\right\}$$

Consider the denominator of N_n which is

$$= -K\bar{\psi}_{n-1}(\eta) + (k-1)\frac{n}{2n+1}\bar{\psi}(\eta) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\bar{\psi}_n(\eta)$$

$$+ i\left\{k\,\psi_{n-1}(\eta) - (k-1)\frac{n}{2n+1}\psi_n(\eta) - \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\psi_n(\eta)\right\}$$

$\therefore$ The denominator of N_n is equal to

$$-K\bar{\psi}_{n-1}(\eta) + (K-1)\frac{n}{2n+1}\bar{\psi}_n(\eta) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\bar{\psi}_n(\eta)$$

$$+ \quad i\ (\text{Numerator of } N_n)$$

Now

$$-K\bar{\psi}_{n-1}(\eta) + (k-1)\frac{n}{2n+1}\bar{\psi}_n(\eta) + \frac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\bar{\psi}_n(\eta)$$

$$= -K\frac{1.3\ldots(2n-1)}{\alpha_n}C_{n-1}(\alpha) + (k-1)\frac{n}{2n+1}\frac{1.3\ldots(2n+1)}{\alpha_n+1}$$

$$C_n(\alpha) + \frac{S_{n-1}(\beta)}{S_n(\beta)}\cdot\frac{\beta}{\alpha_{n+1}}\frac{1.3\ldots(2n+1)}{\alpha_{n+1}}C_n(\alpha)$$

$\therefore K = m^{\cdot 2} = \dfrac{\beta^2}{\alpha^2}$

$$\therefore = \frac{1.3\ldots(2n-1)}{\alpha^n}\cdot\frac{1}{S_n(\beta)}\cdot\left(\frac{-\beta}{\alpha^2}\right)\left\{\beta S_n(\beta)C_{n-1}(\alpha) - S_n\beta\right.$$

$$(\beta)C_n(\alpha)\frac{n}{\alpha} + \frac{n\alpha}{\beta}C_n(\alpha)S_n(\beta) - \alpha C_n(\eta)S_{n-1}(\beta)$$

$$- \quad \frac{1.3\ldots(2n-1)}{\alpha^n}\cdot\frac{1}{S_n(\beta)}\cdot\frac{\beta}{\alpha^2}\left\{\beta S_n(\beta)C'_n(\alpha)\right.$$

$$\left. - \alpha C_n(\alpha)S'_n(\beta)\right\}$$

$$\therefore N_n = \frac{\beta S_n(\beta)S'_n(\alpha) - \alpha S_n(\alpha)S'_n(\beta)}{-[\beta S_n(\beta)C'_n(\alpha) - \alpha C_n(\alpha)S_n'(\beta)] + i[\text{Numerator}]}$$

$$\therefore \quad N_n = -A_n \div \frac{(-1)^n.(2n+1)}{n(n+1)}$$

Consider M_n

$$M_n = \frac{\psi_{n-1}(\eta) - \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\ \psi_n(\eta)}{\overline{\psi_{n-1}(\eta) + \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\overline{\psi_n(\eta)} + } }$$

$$\left\{ \overline{\psi_{n-1}(\eta) - \dfrac{\psi_{n-1}(\eta')}{\psi_n(\eta')}\ \psi_n(\eta)}\right\}$$

$$= \frac{\dfrac{1.3\ldots(2n-1)}{\alpha^{n-1}\beta^{n-1}}\left\{ S_{n-1}(\alpha)S_n(\beta)\dfrac{2n+1}{\beta} - S_{n-1}(\beta)S_n(\alpha)\dfrac{2n+1}{\alpha}\right\}}{\dfrac{1.3\ldots(2n-1)}{\alpha^{n-1}\beta^{n-1}}\left\{ -C_{n-1}(\alpha)S_n(\beta)\dfrac{2n+1}{\beta} + S_{n-1}(\beta)\right.}$$

$$\left. C_n(\alpha)\dfrac{2n+1}{\alpha}\right\} + i\,(\text{Numerator})$$

$$= \frac{\alpha\,S_{n-1}(\alpha)\,S_n(\beta) - \beta\,S_{n-1}(\beta)\,S_n(\alpha)}{-\alpha\,S_n(\beta)\,C_{n-1}(\alpha) + \beta\,S_{n-1}(\beta)\,C_n(\alpha) + i\,(\text{Numerator})}$$

Now

$$\beta S_n(\alpha)S_{n-1}(\beta) - \alpha S_{n-1}(\alpha)S_n(\beta) + nS_n(\beta)S_n(\alpha) - nS_n(\beta)S_n(\alpha)$$

$$= \beta S_n(\alpha)\left\{ S_{n-1}(\beta) - \frac{n}{\beta}S_n(\beta)\right\} - \alpha S_n(\beta)\left\{ S_{n-1}(\alpha) - \frac{n}{\alpha}S_n(\alpha)\right\}$$

$$= \beta S_n(\alpha)S'_n(\beta) - \alpha S_n(\beta)S'_n(\alpha)$$

Similarly

$$\beta S_{n-1}(\beta)C_n(\alpha) - \alpha S_n(\beta)C_{n-1}(\alpha)$$

$$= \beta S'_n(\beta)C_n(\alpha) - \alpha S_n(\beta)C'_n(\alpha)$$

$$\therefore M_n = \frac{-[\beta S_n(\alpha)S'_n(\beta)}{[\beta S'_n(\beta)C_n(\alpha) - \alpha S_n(\beta)C'_n(\alpha)]}$$

$$\frac{-\alpha S_n(\beta)S'_n(\alpha)]}{-i[\beta S_n(\alpha)S'_n(\beta) - \alpha S_n(\beta)S'_n(\alpha)]}$$

$$= -P_n \div \frac{(-1)^{n+1}(2n+1)}{n(n+1)}$$

The expression $\mu P'_n - n (n+1) P_n$ is replaced by Rayleigh for $- \mu P'_n + (1-\mu^2) P''_n$ as these two expressions can be proved to be identical because of the differential equation satisfied by P_n.

Now $P'_n = \dfrac{d}{d\mu} (P_n) = \pi_n$

$P''_n = \dfrac{d}{d\mu} (P'_n) = \pi'_n$

$$\therefore \mu P'_n - (n+1)P_n = -\mu P'_n + (1-\mu^2)P''_n = -[\mu\pi_n - (1-\mu^2)\pi'_n]$$

$$\therefore Y \propto \sum_{n=1}^{\infty} \left\{ (-P_n)[-\mu\pi_n + (1-\mu^2)\pi'_n] + (-1)(-A_n)\pi_n \right\}$$

$$\therefore Y \propto \sum_{n=1}^{n=\infty} A_n\pi_n + P_n[\pi_n\mu - (1-\mu)^2 \pi'_n]$$

Similarly

$$\frac{xZ-zX}{r} \propto \sum_{n=1}^{\infty}(-1)(-A_n) [-\mu\pi_n + (1-\mu^2)\pi'_n] + (-P_n)\pi_n$$

$$\frac{xZ-zX}{r} \propto \sum_{n=1}^{\infty} - A_n [\pi_n\mu - (1-\mu^2)\pi'_n] - P_n\pi_n.$$

According to Love-Rayleigh theory therefore

$$I_1 \propto \left/ \sum_1^{\infty} A_n\pi_n + P_n[\pi_n\mu - (1-\mu^2)\pi'_n] \right|^2$$

$$I_2 \propto \left/ \sum_1^{\infty} A_n[\pi_n\mu - (1-\mu^2)\pi'_n] + P_n\pi_n \right|^2$$

which are also the expressions obtained for the intensity of the scattered light by Mie.

References

(1)   Love : Proc. Lond. Math. Soc. 1899, 30, 308.

(2)   Rayleigh : Proc. Roy. Soc. 1911, 84, 25.

(3)   Mie : Ann. d. Phys. 1908, 25, 428.

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A Water jet Counter

By

R. V. BARAVE,

R. D. SUMMERS [1] has described a simple water-jet counter to demonstrate ionising particles and photons individually. A similar instrument has been constructed in this laboratory, and the very simplicity with which it can be set up, and the fact that two important experiments in Physics are demonstrated thereby, are thought to be sufficient reason for giving a few details of the apparatus.

Figure 1 shows the spark gap and the jet. B & B_1 are two pieces of brass separated by a sulphur or ebonite rod E. C is an ordinary copper rivet soldered to the brass plate and serves as the cathode of the spark gap. The screw S1 controls the distance of the gap while S2 serves as the control electrode affecting the water flow from the glass jet J. Both S_1 & S_2 have 32 threads to an inch and give sufficiently accurate control of the various distances. The jet is made of glass tube 10 mm. bore, drawn to a smaller diameter of 1 mm. at one end.

Water from an independent water tank at a height of four feet is fed through it. A diaphragm is placed so that the water jet strikes it just before it breaks into drops. A high voltage D.C. of 2000 to 3000 volts is obtained from a separate unit and connected across the spark gap through a resistance of 200 megohms as shown in Fig. 2. The spark gap is adjusted till the sparking just ceases. If now a source of alpha particles is brought near the gap, sparks jump across it, and the electrostatic attraction on the water jet is affected, resulting in clicks on the diaphragm. The instrument is sensitive enough to detect in a similar way the ultraviolet rays from a candle flame allowed to shine on the cathode. It may be noted that the experiment can be worked with a charged Leyden jar in place of the high voltage source.

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Sangli.

[1] Rev. Sc. Ins. 6.39, 1935.
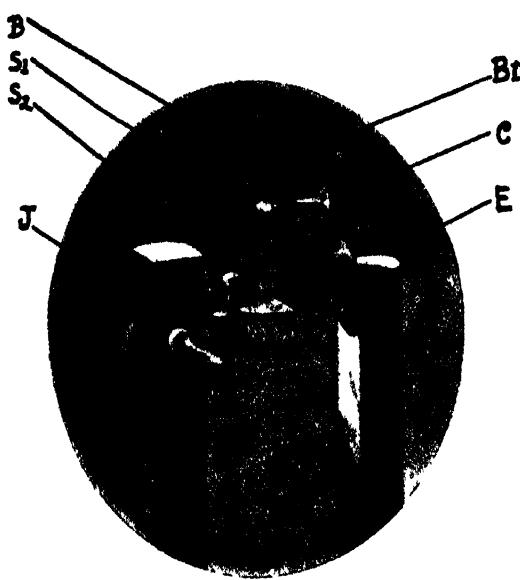
Fig. 1
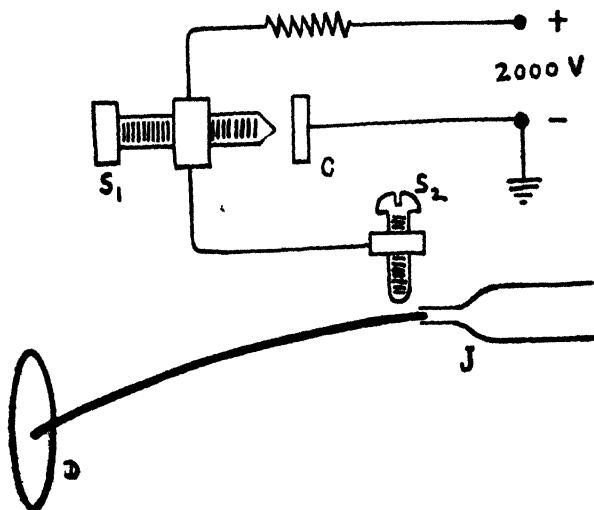
Fig. 2

Determination of the Absolute Value of the Moment of a Magnet

By

V. N. Kelkar

THE deflection and the vibration magnetometers are usually employed to determine the absolute value of the magnetic moment of a bar magnet. The following is a description of another simple laboratory method for the determination of the magnetic moment, wherein a tangent galvanometer has been used.

The principle of the method :—If the field at the centre of the coil of a tangent galvanometer, due to a current, be exactly balanced by the field of a suitably placed bar magnet, the needle will remain undeflected. Under these conditions the following relations can be easily seen to hold good when the bar magnet is placed horizontally along the magnetic east west direction in the plane of rotation of the needle (the coil being in the magnetic meridian plane) :—

(1) $$\frac{2\pi nc}{r} = \frac{2Md}{(d^2 - l^2)^2} \cdots\cdots\cdots \text{(End-on position)}$$

(2) $$\frac{2\pi nc}{r} = \frac{M}{(d^2 + l^2)^{3/2}} \cdots \text{(Broadside-on position)}$$

Here the symbols have their usual significance.*

The Experiment :—The experimental arrangement is shown diagramatically in Fig 1.
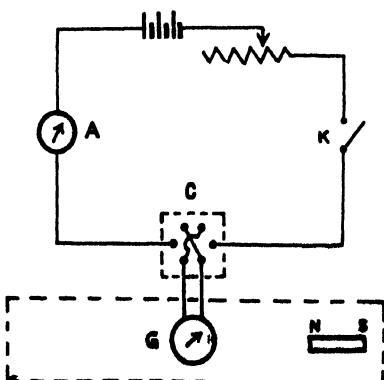
Fig. 1

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* *N.B.*—The magnetising action of the current on the magnet under the experimental conditions will be negligible.

The tangent galvanometer (G) was provided with two detachable arms to support the magnet NS horizontally. The instrument was thus turned into a combination of a tangent galvanometer and a tangent magnetometer. A known current is passed through the galvanometer and the deflection obtained is reduced to zero by placing the magnet at a suitable distance from the needle, in the end-on position. By turning the magnet face to face, reversing the current and the poles, and placing the magnet on the two sides of the galvanometer, a mean of eight readings is obtained for "d" the distance of the centre of the magnet from the needle. These readings are repeated for different values of the current in the coil. The results of a typical experiment are given below. Table I shows the values of the current, the corresponding mean distance "d" and the magnetic moment calculated in each case.

$$n=2; \quad l=4.6 \ cm. \ ; \quad r=7.28 \ cm.$$

TABLE I

Current "A" (Amperes)	Distance "d" (cm.)	Magnetic Moment $M=\dfrac{\pi n}{10 \, r}\left[\dfrac{A \, (d^2-(l^2)^2}{d}\right]$ (erg gauss^{-1})
0.5	25.1	638
0.6	23.8	647
0.7	22.8	659
0.8	21.8	653
0.9	21.0	652
1.0	20.3	650
1.1	19.7	649
1.2	19.1	640
1.3	18.7	648
1.4	18.3	650
1.5	18.0	660
2.0	16.4	647
2.5	15.4	654
		Mean = 650

The most probable value of "M" = (650±1) erg. gauss^{-1}.

The usual magnetometer method gave a value of 666 erg. gauss^{-1} for the moment of the same magnet.

It may be remarked in passing that instead of nullifying the deflection of the needle when the current is on, any particular deflection due to a current may be reproduced by adjusting the position of the magnet after the current is switched off. The details of the experiment and the method of calculation are the same as before.

Author's thanks are due to Prof. M. W. Chiplonkar for his keen interest in the subject.

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NOTES AND NEWS

How Could We Be Bridge-Builders?

IF there was at any time a greater need for bridge-building in the world, it was now. If there was at any time a greater need of bringing into being a class of bridge-builders in the world, it was to-day. We have, so far, laid a great emphasis on analysis and specialization. The present may be described as an age of specialization. Specialization has, no doubt, a place in the evolutionary scheme and should, by no means, be under-rated but it has a tendency to narrow and cramp the mind. This tendency requires to be corrected and counterbalanced by the synthetic faculty of the mind. It is, therefore, necessary for the specialist to keep his eyes wide open and see the trend of thought in other departments of knowledge and in other spheres of life. This will act as a corrective and enable him to broaden his mind, give right values to all things and see them in their proper perspective.

If a student of one branch of science keeps his mind open and makes a definite effort to find out what is happening in spheres outside his own, then he will know that, of late, a type of scientist is emerging who no longer holds the narrow orthodox materialistic view of the nature of the atom and of the ultimate constitution of the physical world. Modern scientific research, instead of materializing our world, has dematerialized it. Matter is resolved into energy and matter and energy are now inter-convertible terms.

He will also notice that the distinction between "organic" and "in-organic" has now disappeared ; the barriers between the two have been broken down by modern science. There is nothing in nature which is not living in the sense that it is sustained and penetrated by one All-pervading life.

He will, further, see that a new interpretation is given of the evolutionary process in terms of an inner compelling energy which is supposed to be present in the unfolding life and to shape the outer form to its own vital demands. And therefore evolution is no longer a mechanical but a vital process. The world-process is not looked upon as a mere "record of the simple reactions of matter upon matter, but the living and purposeful story of the unfolding of indwelling life."

These researches in physical and biological sciences have brought about a revolution in evolutionary thought and shifted its centre of gravity from a purely materialistic to a larger conception of life. "In almost every direction there is a general reaching outward towards a larger life—a growing appeal under a hundred different shapes to a Higher Vital Principle."

The most characteristic feature which is noticeable at present in magazines like "Nature," "Current Science" and others is the great prominence given to the discussion of subjects like science and ethics, science and religion, science and social relations, etc.—subjects which were tabooed or practically ignored or considered to be quite outside their purview a few years ago. A perusal of these and other cultural magazines will help any person to know the new trend in the thought of the world to-day.

Bridge-building is an art and science. A person who is dissatisfied with the present state of affairs in the world, who wishes to find out the causes which have led to the present chaos, who wishes to do his little bit to the solution of the complicated problems which face humanity, gradually grows into a bridge-builder; for, he will be the person who will first begin to bridge the gulf between his own thoughts, emotions and actions and thus harmonize them ; then, he will act as a bridge between the present and the past, between science and religion, and between science and society. He will not live in a water-tight compartment of his own but will consider knowledge as one organic whole and link up the different branches of science, perceive relationships between science and other branches of knowledge and thus bring about a great synthesis of knowledge. In this very process of synthesis and bridge-building he will himself unconsciously grow into a cultured man. And then as a cultured man he will not rest until he has built up bridges between man and man, man and woman, youth and age, between community and community, class and class, nation and nation and faith and faith.

This is the task confronting the educated man and woman of the present day. Let our universities see that their alumni grow up into cultured individuals and loving, compassionate human beings, willing to share one another's sorrows and burdens and anxious to co-operate with other people to convert the present war-ridden world of ours into a beautiful temple of learning and wisdom and a happy home of peace and bliss.

<div align="right">D.D.K.</div>

Book Reviews

An Introduction to Analytical Geometry and Calculus.—By T. K. Raghava-
chari M.A., Oxford University Press, 1941, pp. xx × 192. (No price
given.)

The South Indian Universities have recently introduced elements of
Analytical Geometry and Calculus in their Intermediate courses and this
book by Professor Raghavachari of Madras Christian College is designed
to cover the syllabus. There is a short historical introduction, which is
both instructive and stimulating ; this is followed by about 90 pages of
elementary analytical geometry of the straight line and the circle (Ch. I
—V) and another 90 pages or so of Differential and Integral Calculus
(Ch. VI—XI). In the latter part, the differentiation and integration of
simple algebraic and trigonometric functions is explained together with
simple applications. One misses any discussion of exponential and logari-
thmic functions, but that is no doubt due to the syllabus prescribed by the
South Indian Universities.

In an introductory course on Calculus, no two authorities will agree
exactly at every step regarding the rival claims of geometrical intuition
and analytical rigour. The teacher must everywhere be guided by his
own experience of his students' maturity and their previous training. It
is therefore all the more pleasing to note that the reviewer, who has some
experience both as a teacher and an author, finds many points of
agreement with the author of this book. The treatment is lucid and sound
and there is no doubt that the book will be found of great use by beginners.
The syllabus of the University of Bombay covers more ground, but even
here the book may be read with advantage as a first course, especially if
elements of Analytical Geometry and Calculus are introduced in the
First Year Course.

The general appearance and printing of the book are pleasing.

K. R. G.

A First Course in Algebraic Geometry.—By B. B. Bagi, M.A.

A striking feature of the book is an almost complete absence of the
Calculus method (except for the parabola) in finding the equations of
the tangent and the normal. The 'chord-method' is unnecessarily
laborious and the calculus method might have been used at least as an
alternative.

The angle between straight lines joining two points to the origin is
found on p. 32 and the conditions of their perpendicularity and coincid-
ence are deduced. All this is done much before the author has taken up

the general theory of the Straight Line. These results appear to be an unnecessary strain on the memory and may have been given at this stage, if at all, in the form of examples.

There are some minor omissions from the point of view of a candidate preparing for an examination. For instance, the bisectors of the angles between two straight lines are found on p. 73, but for distinguishing between them, the student is referred to a solved example. No doubt, this makes the ideas clear, but the theory becomes incomplete. Again the equation of the tangent to the circle $x^2+y^2+2gx+2fy+c=0$ at a point $(x, y.)$ on it is given *without* proof.

A commendable feature of the book is that the author has made the idea of the equation of a curve quite clear. This is very important as many students, after learning the subject for a year, are not able to say in clear terms what an equation really means, although they can quote all sorts of equations. The students are required to find out the equations of particular straight lines on p. 41 from first principles, although the general theory of the Straight Line begins on p. 53. This ought to make the students previously familiar with the idea of an equation.

The book is written in a clear and simple style and a large number of examples are given, both solved and unsolved. Although it does not appear to be an improvement upon the existing text books both from the point of view of presentation and subject matter, generally speaking, it ought to be quite useful to the students preparing for the Intermediate Arts and Science examinations of this University, a purpose for which it was meant.

<div align="right">V. D. Thawani</div>

Intermediate Electricity—By Robert W. Hutchinson, M.Sc., University Tutorial Press, London, 1941. Price 12s. 6d.

The last quarter of a century and more may be said to be an epoch of rapid progress in the science of physics. Our conceptions about the nature of physical phenomena have undergone tremendous evolution since the year 1900. The growth of new ideas has led to two distinct divisions in physics, *viz.*, the classical physics and the modern physics.

During the period of growth of new physics, classical text-books in physics have either been rewritten or reprinted to cover the new ground. But only a few of these have been so altered as to offer a treatment different from the traditional mode. The present book can be said to come under this rare class. The subject matter of the book is electricity and magnetism, and this is particularly a branch of physics which has been rapid strides of progress in fundamental ideas as a result of new researches and inventions.

The phenomena in magnetism and electricity are so interdependent on each other that it is impossible to treat these subjects separately in water-tight compartments, as found in almost all classical text-books. The author, seeing this difficulty, departs from the conventional mode to treat from the beginning the ideas about the structure of matter, the electric and electronic currents and the accompanying phenomenon of magnetism. Naturally some of the crucial experiments in later physics

have been cited in support of these ideas. The subject is then developed on a logical basis. The scheme will readily appeal to those who have followed the modern trends in physics.

The author's aim in writing this book is to supply the needs of the Intermediate classes, but the details included seem to be definitely in advance of the Intermediate standard of many Indian Universities, unless selective omissions are made which is not desirable in the interest of the sequence. The book may not be enough for the B.Sc. standard, though it may come up very near to its expectations.

The method of treatment is rather exhaustive; far too lengthy but effective explanations have been given to convey the meaning of fundamental ideas. A number of possible alternatives to classical experiments have been included and typical numerical examples solved—a feature which has enhanced the value of the publication. For these reasons the book is likely to serve more as a treatise than a text-book. It can therefore be recommended for reading to teachers and students alike, as companion to a regular text-book on Electricity and Magnetism.

N. R. T.

Books Received

Annual Report—Twentieth, of the Institution of Engineers (India), Bombay Centre.

Bulletin and *Annual Report*—Sixteenth, of the Texas Technological College, Texas.

Hydrogenated Coal-Tar Chemicals, 98 *to* 100% *Purity* ; Barrett & Co.

Lecture on :

  Chromatographic Analysis by A. H. Cook, Ph.D., D.I.C., A.I.C.

  The use of the Spekker Photo-Electric Absorptiometer in Metallurgical Analysis by E. J. Vaughan, M.S., A.R.C.S., F.I.C. Published by the Institute of Chemistry of Great Britain and Ireland.

Technical Paper ·

  No. 308—Braking Distances of Metre Gauge Trains by E. W. Baker, M.I.E.E., M.I.R.S.E., A.M.I.Mech.E., Signal Engineer, A. B. Railway, India.

  No. 309—The Section and Armour of a Guide Bank for the Training and Control of the Great Alluvial Rivers by K. B. Ray, B.E., M.I.E. (Ind.), Deputy Chief Engineer E. B. Railway.

  No. 310—The Heat Treatment of Steel and Iron with Notes on Comented Carbide Tools by C. W. Clarke, A.M.I.C.E., A.M.I.M.E., Mechanical Engineer, G.I.P. Rly.

Acknowledgments

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[BIOLOGICAL SCIENCES, INCLUDING MEDICINE: NO. 11]

CONTENTS

A CONTRIBUTION TO THE STUDY OF THE ECOLOGICAL FOLIAR ANATOMY OF INDIAN PLANTS

By

J. F. R. D'ALMEIDA, B.A., M.SC., AND JAYANT L. DESAI, M.SC.,

St. Xavier's College, Bombay

(With twenty-one plates)

INTRODUCTION

G ENERAL REMARKS.—In the present treatise an attempt is made to study the anatomical features of the leaves of some of our Indian plants with reference to the environment. Apart from references appearing in general treatises (12, 13, 17, 18, 47, 53), enough of work of this nature has been done in other countries (9, 11, 19, 21, 22, 31, 34, 43) and in some instances the interpretations of the structures observed are sought to be supported by experiment (19, 31, 41). But in India, with the exception of Sabnis' contributions on the anatomy of Desert plants (42) and of the Indus Delta (5), and Mullan's work on the physiological anatomy of the halophytes (including the mangrove) (38, 39, 40), very little anatomical work has been attempted. An anatomical study of the leaves with reference to the environment acquires a special significance in the case of Indian plants in view of the fact that in India, as Saxton (44, 45) has pointed out, owing to the alternately wet and dry monsoon climate, two different sets of conditions prevail during the year with the result that one and the same plant is exposed to altogether opposite environmental conditions and would naturally be expected to react to these conditions. As far as the present writers are aware, this aspect of our Indian plants, dealing with the anatomical modifications induced by periodic changes in the environment, has hardly been touched upon. The present work which restricts itself to the leaf modifications in this respect is an attempt in this direction.

The material for the work was obtained from Salsette, an area representative of a typical monsoon region. The plants dealt with include some of the deciduous and evergreen trees and shrubs in our jungles, some climbers and a few herbs taken from diverse habitats. As we have Mullan's authoritative work on halophytes, these are deliberately excluded from the present study.

II (1)

Arrangement and Method.—In the body of this work the plants are treated under the following heads :—

1. Deciduous trees and shrubs,
2. Evergreen trees and shrubs, and
3. Herbs.

In the case of the first two groups, as transitions occur, it is not always easy to allocate the plants. In such instances the plants are placed in that category to which they more frequently conform. The description of the leaf of each plant is preceded by a note on the general characteristics of the plant, gathered from personal observation as well as from accounts appearing in Indian Floras and other allied literature (2, 3, 4, 10, 19, 24, 26, 30, 36, 37). The descriptions of the external features of the leaf are also based on similar sources. The descriptions of internal structures are illustrated by camera lucida drawings. As far as possible the interpretations of the modifications observed as well as the various conclusions drawn, are embodied in the descriptions of the individual plants. The study of the internal structures is almost entirely the contribution of the present writers. The conclusion at the end summarizes the results and serves as a synopsis of the work. For the purpose of anatomical examination, fresh leaves or leaves preserved in alcohol were employed and hand sections taken. In some instances, microtome sections gave good results.

Some explanation seems to be called for with regard to the terminology of "xerophytism" used in this treatise. For obvious reasons we have been unable to adhere to the distinctions laid down by Thoday (50). Though the term "xerophytic" would more strictly be applied to features characterstic of xerophytes, *i.e.* plants of dry habitats, in the present context the term is frequently used to imply also those features of plants not necessarily xerophytes which show a likeness to those of plants actually growing in dry localities and which would according to Thoday be more correctly termed "xeromorphic." In other words, the terms "xerophytic" and "xeromorphic" used in the text are interchangeable. We have, however, adopted the term "xeroplastic" to indicate features which can be proved by experiment or otherwise to be the direct effects of a dry environment.

DESCRIPTION

1. DECIDUOUS TREES AND SHRUBS

Gossampinus malabarica Merr. (=*Bombax malabaricum* DC.)

It is a deciduous tree with a straight, erect, buttress trunk, and wide-spreading branches. The stems and branches are armed with conical prickles (10). The leaves which are palmately compound 3–7 foliate, are shed piecemeal, the leaflets and petiole breaking off at the joints and falling separately. Leaf shedding usually begins in dry situations in December, and by the end of the month the trees are bare. In moist situations, however, leaf-fall may be postponed till March. New leaves appear in March or April. Flowering takes place in the leafless period. But if the tree is in leaf the flowers are not so numerous (8, 36, 51).

PLATE I
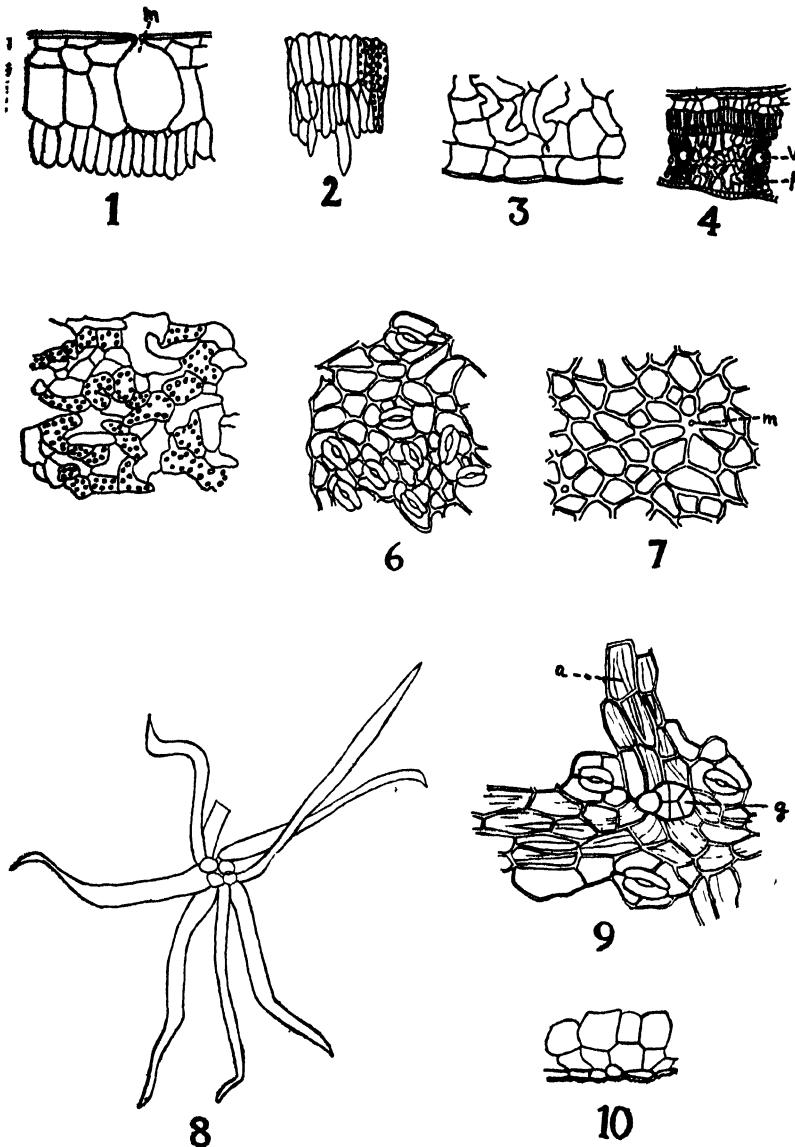
Figs. 1–10.—*Gossampinus malabanica* Merr.: Fig. 1. T. S. of a leaflet showing a portion of upper epidermis with mucilage cell (*m*) and part of palisade. (× 240); Fig 2. T. S. of leaflet showing palisade tissue. (× 240); Fig. 3. T S. of leaflet showing lower epidermis. (× 240); Fig. 4. T. S. of leaflet (semi-diagrammatic): *V*, vascular bundle, *p*, bridges. (× 80); Fig. 5. T. S. of leaflet showing spongy tissue. (× 240); Fig. 6. Lower epidermis (surface view). (× 240); Fig. 7. Upper epidermis (surface view). (× 240); Fig. 8. Peltate hair. (× 240); Fig. 9. Lower epidermis (surface view) showing anastomising tracts with striations (*a*) and a glandular hair (*g*). (× 240); Fig. 10. T. S. of leaflet showing lower epidermis and underlying mesophyll with uneven toothed cuticle caused by striations. (× 240).

N.B. – The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

The Leaf :

(*A*) *External Features.*—The leaves are large, digitate ; leaflets 3-7, entire, 3-7 ins. long, glabrous, pinninerved, reticulately veined, lanceolate or oval (10).

(*B*) *Internal Structure.*—(Figs. 1-10). The leaflets show a dorsiventral structure (Fig. 4). Both the upper and lower epidermis consist of more or less tabular cells, which, in surface view, appear to have somewhat straight walls (Figs. 6, 7). The upper epidermis is many-layered (2 to 4-layered in the leaves examined) with the cell-wall well thickened and cutinized. Flask-shaped mucilage cells occur in the upper epidermis. These have minute apertures opening on the surface (Figs. 1, 7, *m*). The walls of the epidermal cells of both the upper and lower sides become thickened and cutinized as the leaf gets older. The upper epidermis is devoid of stomata (Fig. 7). Stomata are present on the lower epidermis. They are confined to definite stomatal areas bounded by stomateless anastomosing tracts. The latter are made up of slightly elongated epidermal cells which appear strongly striated in surface view (Fig. 9, *a*) due to the development of outwardly projecting cuticular ridges (Fig. 10). These stomatal areas, as we shall see later, correspond internally to the photosynthetic units into which the mesophyll of the leaf is divided. Hairy covering in the shape of stalked stellate hairs occurs both on the upper and the lower surface in very young leaves (Fig. 8). In slightly older leaves they are seen to be confined to the upper surface only. They are altogether absent from both the surfaces as the leaf gets still older. Glandular hairs (Fig. 9, *g*) occur on the lower epidermis. Each gland is multicellular and consists of a rounded head made up of four cells placed on a stalk. These glandular hairs are mostly confined to the stomateless tracts. The mesophyll is made up of a palisade tissue, two cells deep (Fig. 2) and a spongy layer composed of loosely arranged irregular-shaped radially branched cells (Fig. 5). The mesophyll, as we have already mentioned above, is broken up into distinct photosynthetic areas bounded by bridges of cells extending from epidermis to epidermis (Fig. 4, *p*). In these bridges are embedded the veins (*v*). Each such photosynthetic area is thus actually a vein islet. It should be noted that the photosynthetic tissue on the whole is loose. Cells composing the bridges serve as storage cells for water and, as they extend from epidermis to epidermis, furnish the mechanical support that is lacking owing to the looseness of the mesophyll. The strong reticulate venation, embedded in the bridges of tissue, which extend from epidermis to epidermis, while making for the rigidity of the leaf, ensures a perfect circulation of the fluids (18) as well as brings about an isolation of the vein islets. In very old leaves the cells of the tissue forming the bridges as well as also the epidermal and palisade cells may become charged with brown contents (tannin). The leaf is typically xeromorphic.

Lannea grandis Engl.   (=*Odina Woodier* Roxb.)

This is a common deciduous tree, occurring in the mixed deciduous forests of India, Burma and the Andamans. The leaves commence falling in November and from December–January to May–June, the tree is leafless. Flowers appear and bloom in March–April, whilst the tree is bare of leaves (51). In some parts of peninsular India, especially

the east side, the tree remains in leaf almost throughout the year (8). But on the whole the leafless period corresponds to the greater part of the dry season.

The Leaf:

(*A*) *External Features.*—The leaves are crowded about the ends of the branches. They are 10–18 in. long, compound imparipinnate with a slender angled rachis and membranous leaflets which are green above and brown beneath (when dry), 3–5 pairs and an odd one, 3–6 by 1–2 in. ovate oblong, acuminate glabrous, shining, tinged with pink when young, base acute or rounded, often oblique ; main nerves 6–8 pairs (10).

(*B*) *Internal Structure.*—(Figs. 11–16). The upper epidermis consists of tabular cells most of them with dark contents. The outer and side walls are considerably thickened (Fig. 11) and appear striated in surface view (Fig. 14) due to cuticular ridges which project outward. There are no stomata on the upper surface. The cells of the upper epidermis are pitted. The lower epidermis also consists of tabular cells but with more or less wavy outlines (Fig. 16). The cell-walls are also thickened as in the upper epidermis but to a less extent. Most of the cells have brown contents, probably tannin. The stomatal frequency is 560 per 1 sq. mm. The stomata are raised, with the guard-cells thick-walled and having strong cutinized ridges which provide a relatively large external air chamber (Fig. 15). The palisade tissue consists of two layers of elongated cells the outer one of which has dark contents. In the outer layer there are few or no chloroplasts. The inner layer contains chlorophyll. Here and there between the two layers of the palisade cells are large round cells containing crystals of calcium oxalate (Fig. 12). The spongy tissue consists of oval cells more or less loosely arranged. The walls of both palisade and spongy cells are thickened somewhat. The sheath round the vascular bundle is also found to have dark cell contents. Lying in the mesophyll are tracheides of large dimensions and approaching the isodiametric form (Fig. 13). These are obviously water storage tracheides (19) which terminate the vascular bundles. The structure is xeromorphic.

Semecarpus Anacardium Linn.

Semacarpus Anacardium Linn. is a moderate-sized deciduous tree with leaves crowded at the ends of branches (49). It occurs throughout the Presidency in dry forests (10).

The Leaf:

(*A*) *External Features.*—Leaves alternate, simple, quite entire, coriaceous, 7–24 by 4–12 ins. obovate oblong, rounded at the apex, glabrous above, ashy grey or buff and more or less pubescent beneath and with cartilaginous margins, base rounded, cordate or cuneate, sometimes shortly auricled ; main nerves 15–25 pairs making a large angle with the costa, sometimes nearly horizontal, prominent on both surfaces (10).

PLATE II

11   12   13

14   15   16

17   18   19   20
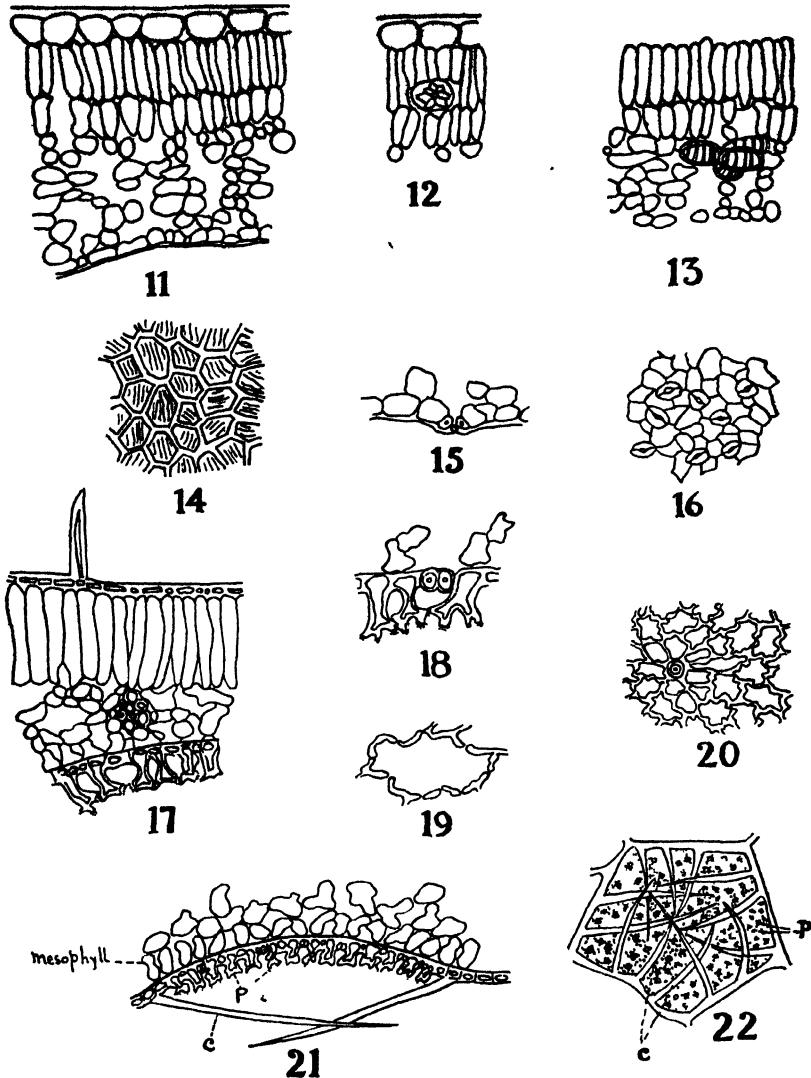
mesophyll   21   22

Figs. 11–16.—*Lannea grandis* Engl. : Fig. 11. T. S. of leaflet. (× 240); Fig. 12. Upper epidermis with a portion of palisade layer in T S. with a cell containing crystal. (×240); Fig. 13. Mesophyll in V. S. containing water storing tracheides. (× 240); Fig. 14. Upper epidermis (surface view) with striations. (× 240); Fig. 15. Stoma in V. S. (× 540); Fig. 16. Lower epidermis in surface view (×240)

Figs. 17–22.—*Semecarpus Anacardium* Linn. : Fig. 17. T. S. of leaf. (× 240); Fig. 18. Lower epidermis in T. S. showing stoma and papillose epidermal hairs (P). (× 540); Fig. 19. Upper epidermis in surface view showing pits. (× 720); Fig. 20. Upper epidermis (surface view) showing hair base. (× 240); Fig. 21. T. S. of the lower side of the leaf (diagrammatic) showing the shallow stomatal chambers lined by papillose epidermal cells (P) and covered by a loose thatching of clothing hairs (C). (× 240); Fig. 22. A shallow stomatal chamber (corresponding to vein-islet) in surface view (diagrammatic) with the clothing hairs extending inward to form a loose thatching through which the cuticular teeth-like projections of the branched extremities (P) of the papillose hairs may be seen. (× 25).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

(*B*) *Internal Structure.*—(Figs. 17-22). According to Solereder (47) the leaf-structure of the *Anacardiaceae* has not been subjected to thorough investigation. Hence it may be presumed that the data given in this description as well as for the other *Anacardiaceae* dealt with in this work are new. The epidermis of the upper surface (Figs. 17, 20) consists of tabular cells which appear wavy in outline in surface view and are rather thick-walled, with pits on the lateral and inner walls (Fig. 19). Stiff unicellular hairs are found mostly on veins. No stomata occur on the upper surface. The lower epidermis consists, for the most part, of cells elongated vertically outward so as to form tubular hair-like prolongations, which become forked and branched, and form a close felt-like canopy protecting the stomata which are found distributed among the bases of these hairs. The ultimate branches of these forked papillose cells are provided with cuticular teeth-like projections which meet similar projections on the branches of the neighbouring cells and thus make the canopy more efficient in providing a dead air space for the stomata (Figs. 17, 18). These papillose epidermal cells are rather thick-walled, and a nucleus is seen in each cell. On a closer examination of the section, it is noticed that the under side of the leaf is thrown into undulations (Figs. 21, 22), each depression corresponding to a vein-islet. These depressions, since they contain a number of stomata and are lined by the papillose epidermal cells (*P*) which serve as screens to the stomata, function as shallow stomatal chambers. A further protection is afforded by a number of elongated hairs (*C*) which occur mostly on the veins and stretch across horizontally forming a second somewhat loose roof or thatching over the depressions. In the papillose cell, we have an epidermal cell which combines in itself the double function of protecting the inner tissue (mesophyll) and of screening the stomata. The mesophyll consists of a single layer of rather thick-walled palisade cells with dark contents and a ordinary moderately loose, thick-walled, spongy parenchyma. Vascular bundles are enclosed in bundle sheaths which at the larger veins extend from epidermis to epidermis and are often sclerenchymatous. The structure is xeromorphic.

Erythrina indica Lam.

It is a moderate-sized deciduous tree, reaching 60 ft. in height with stem and branches armed with small conical dark-coloured prickles. The tree is common throughout the Konkan. The old leaves are shed early in autumn. It flowers from February to May before the young leaves issue (10, 36).

The Leaf :

(*A*) *External Features.*—The leaves are pinnately trifoliate, 6-12 inches long, deciduous, with the petioles readily disarticulating ; leaflets 4-6 by 3½-5 ins. (the terminal leaflet the largest), membranous, broadly rhomboid-ovate, acute or acuminate, more or less stellately pubescent when young, glabrous when mature (10).

(*B*) *Internal Structure.*—(Figs. 23-27). Solereder (47) mentions that the anatomy of *Erythrina* has received attention from Debold (14). The transverse section of the leaflets (Fig. 2) shows both the upper and lower epidermis to be made up of tabular cells with very wavy outlines (Figs.
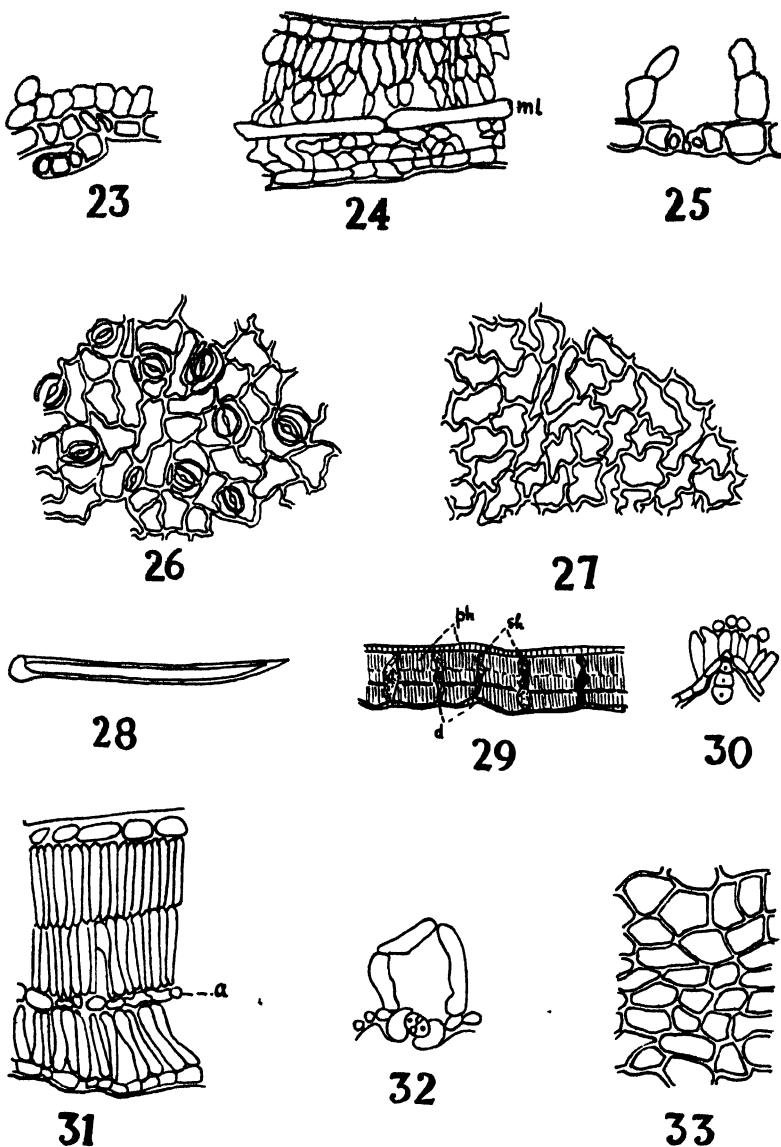
Figs. 23-27.—*Erythrina indica* Lam : Fig 23. T. S. of the lower portion of the leaflet showing glandular hair on the under side . (× 540) : Fig. 24. T S. of leaflet : *ml.* middle layer. (× 240) ; Fig. 25. Stoma in V. S. (× 240) ; Fig. 26. Lower epidermis (surface view). (× 240) ; Fig. 27. Upper epidermis (surface view). (× 240).

Figs 28-33.—*Butea monosperma* O. Kuntze : Fig. 28. A hair from the lower surface of the leaflet (× 240) ; Fig. 29. T. S. (diagrammatic) of leaflet showing depression (*d*) and sheaths (*sh*) enclosing vascular bundles. (× 80) ; Fig. 30. Glandular hair on lower epidermis. (× 240) ; Fig. 31. T. S. of the leaflet : *ml.*, middle layer. (× 240) ; Fig. 32. Stoma in T. S. (× 540) ; Fig. 33. Upper epidermis (surface view). (× 240).

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26, 27) and with thick walls, the upper epidermal cells being slightly more thick-walled than the lower. Stomata are confined only to the lower surface. They are not sunken. They are of the ordinary type with both inner and outer cuticular ridges prominent so that the front and the back cavities become quite distinct (Fig. 25). Uniseriate glandular hairs occur on the lower surface (Fig. 23). The mesophyll appears bifacial and consists of two to three layers of elongated palisade cells separated from the spongy parenchyma by a middle layer of transversely elongated cells with more or less clear contents. This middle layer has been recorded to occur in several *Papilionaceae* (47). The spongy parenchyma is made up of irregular shaped isodiametric cells somewhat loosely arranged. The structure is obviously xeromorphic.

Butea monosperma O. Kuntze (=*B. frondosa* Koenig)

It is a deciduous tree growing in mixed forests. It is common throughout the Bombay Presidency. The tree has an irregular crooked trunk and irregular branches. Leaf-shedding begins at the end of November or beginning of December and by the end of January some of the trees are leafless or nearly so. Flower buds appear on the bare branches in January and flowering continues according to locality up to the end of March or even to the end of April. Many plants retain their leaves particularly on the lower branches during the flowering season, up to the end of March. New leaves appear in April or early in May and are a delicate fresh green colour (4, 8, 49, 51).

The Leaf:

(A) *External Features.*—The leaves are compound, pinnately 3-foliate; leaflets coriaceous. Old leaves glabrous above and finely silky below ; this silky covering gives the leaves a peculiar greyish appearance when seen from a distance. The net-work of veins stands out very conspicuously beneath in the leaflets. Terminal leaflet 4–8 ins. long and about as broad as long, broadly obovate from a cuneate base ; lateral leaflets smaller, 4–6 by 3–4 ins. obliquely rounded at the base (4, 10).

(B) *Internal Structure.*—(Figs. 28–33). Solereder (47) mentions *Butea* as one of the genera of the *Papilionaceae* investigated by Debold (14). A transverse section of the leaflet (Fig. 31) shows an upper epidermis with much thickened and strongly cutinized walls specially on the outer side. The lower epidermis is less thickened, though of course, to an appreciable extent. The upper epidermis (Figs. 31, 33) consists of tabular cells more or less irregular in outline when viewed from the surface. Sometimes there is a one-layered hypoderma beneath the upper epidermis as previously recorded (5, 47) for many plants of this order. The lower epidermis also consists of tabular cells with irregular (not quite wavy) outlines in surface view. The guard cells of the stomata (Fig. 32) on the lower epidermis are surrounded by a pair of subsidiary cells which project outward and together form an external air chamber over the stomata. Each guard-cell has cutinized ridges corresponding to its upper and lower edges and thus the front and back cavities are quite distinct. The front and back cavities together with the external air chamber formed by the subsidiary cells have the effect

of impeding the passage of gases. Clothing and glandular hairs occur on the lower surface. The clothing hairs (Fig. 28) are thick-walled and unicellular. They usually arise in the depressions that are to be found below the veins, and are thus associated with veins. They are appressed and lie against the surface of the leaf. Glandular hairs (Fig. 30) occur both on the general surface as well as in the depressions. They are club-shaped and uniseriate. The mesophyll is isobilateral. It is made up of palisade cells consisting of three layers (Fig. 31) two of which lie on the upper side and are separated from the lowermost layer next to the lower epidermis, by a layer of smaller cells (*a*) known as middle layer which runs parallel to the surface. This middle layer has been referred to by Solereder, Vol. I, p. 258, (47) as occurring in several plants of the order, including *Butea*. The middle layer differs in cell contents. In older leaves it is brown in colour probably due to the presence of tannin. The only resemblance that the lower palisade layer has with the spongy tissue which it has replaced is that it is of a loose texture. The veins enclose distinct photosynthetic areas (Fig. 29, *ph*) and they are embedded in sheaths (*sh*) of clear cells which extend from epidermis to epidermis and often become sclerenchymatous. Where these sheaths meet the lower epidermis, the latter shows a depression (*d*) in which, as already pointed out, are the hairs referred to above. The leaflets are thus typically xeromorphic : An epidermis with strong walls, the mesophyll solely made up of the palisade cells, a strong network of veins—which with its sclerenchymatous sheaths extending from epidermis to epidermis affords an effective support to the lamina and ensures perfect circulation of the fluids and isolates the photosynthetic units— and lastly the characteristic structure of the stomata and their position with reference to the subsidiary cells which provide an additional air chamber, are all xeromorphic characters.

Butea superba Roxb.

Butea superba Roxb. is a gigantic woody, deciduous climber with a stem as thick as a man's leg. It flowers between March and April. The pods ripen between June and July and the leaves are shed between February and May (4).

The Leaf :

(A) *External Features.*—The leaflets are much larger than those of *Butea monosperma*, usually 12–18 ins. in length attaining quite 20 ins. in young plants (4).

(B) *Internal Structure.*—(Figs. 34–38). The leaf differs from that of *Butea monosperma* in being bifacial, the mesophyll being differentiated into a single layer of elongated palisade cells and a spongy parenchyma of loosely arranged more or less isodiametric cells (Fig. 34). The epidermal cells are tabular with walls cutinized and considerably thickened so that the lumina are much reduced. In surface view (Figs. 36, 37, 38) they appear more wavy in outline than those of *B. monosperma*. The stomata have strong cutinized ridges. The hairs (Fig. 35) are strong, straight and erect, unlike those of *B. monosperma* which are appressed and lie against the surface of the leaf. The structure is xeromorphic.

PLATE IV
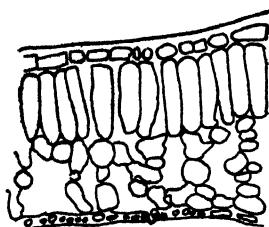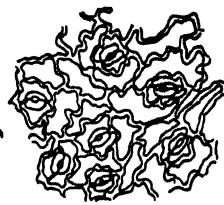
34 **35** **36**
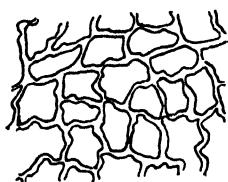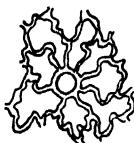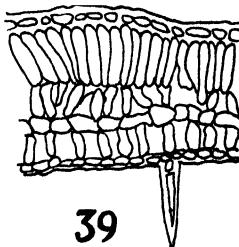
37 **38** **39**
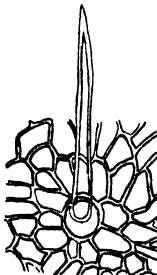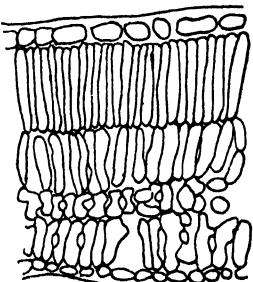
40 **41** **42** **43**
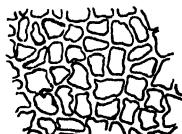
44 **45** **46**

Figs. 34–38.—*Butea superba*. Roxb.: Fig. 34. T. S. of leaflet. (× 240); Fig. 35. A hair. (× 240); Fig. 36. Lower epidermis (surface view). (× 240); Fig. 37. Upper epidermis (surface view). (× 240). Fig 38. Hair base. (×·240).

Figs. 39—42.—*Cylista scariosa* Roxb: Fig. 39. T. S. of leaflet. (× 240); Fig. 40. Upper epidermis (surface view). (× 240); Fig. 41. Lower epidermis (surface view). (× 240); Fig. 42. Stoma in V. S. (× 540).

Figs. 43–46.—*Pongamia glabra* Vent.: Fig. 43. T. S. of leaflet. (× 240); Fig. 44. Stoma in vertical section. (× 540); Fig. 45. Lower epidermis (surface view). (× 240); Fig. 46. Upper epidermis (surface view). (× 240).

N.B—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

Cylista scariosa Roxb.

This is a very common woody twiner found in the jungles of the Bombay Presidency and growing in open places in deciduous monsoon forests (10, 49).

The Leaf :

(A) *External Features.*—Leaves pinnately 3-foliate ; leaflets 2-4 by 1½-2¼ ins. (the terminal, rhomboid-ovate ; the lateral, slightly smaller, very obliquely ovate), acute, clothed with soft velvetty pubescence above, densely downy and prominently reticulately veined beneath (10).

(B) *Internal Structure.*—(Figs. 39-42). This has been included in the list given by Solereder (47) of the plants investigated by Debold (14). The upper epidermis (Figs. 39, 40) consists of thick-walled, strongly cutinized, tabular cells which appear somewhat wavy in outline when viewed from the surface. There are no stomata on the upper side. The under surface, as seen in transverse section, appears to be slightly undulated. The cells of the lower epidermis (Figs. 39, 41) are relatively less thick-walled. The stomata have no special relation to the undulations and are found both on the ridges and on the furrows. They are of the ordinary type with prominent cuticular ridges (Fig. 42). Hairy covering (Figs. 39, 40, 41) consists of strong tapering uniseriate hairs made up of a short basal cell and a long terminal one forming the greater part of the hair. Pear-shaped multicellular glandular hairs also occur and are generally found in the pits. The mesophyll is isobilateral and made up of three layers of elongated palisade cells, the two upper layers being separated from the lowermost by a middle layer of smaller cells having the long axis parallel to the surface. The structure is xeromorphic.

Pongamia glabra Vent.

Pongamia glabra Vent. is a moderate-sized, nearly evergreen tree, reaching 40–60 ft. high, and has a spreading crown. It is found to occur throughout the greater part of India and Burma, chiefly along the streams especially near the coast. It is wonderfully adaptable as regards locality. It is almost evergreen, but if leafless or nearly so, it is for a short time in May. Bourdillon (6) says it drops its leaves several times during the year. The tree is in flower from April to June (51).

The Leaf :

(A) *External Features.*—Leaves imparipinnate, 5-9 ins. long, pale-green ; leaflets opposite 5-9 (usually 5), 2½-5 by 1½-3 ins., ovate oblong or elliptic, acute or (usually) shortly acuminate, glabrous, base acute or rounded, main nerves 6-8 pairs prominent beneath (10).

(B) *Internal Structure.*—(Figs. 43-46). *Pongamia* has been mentioned by Solereder (47) in the list of the *Dalbergiae* investigated by Kopff (28). Both the upper and lower epidermis consist of tabular cells, with wavy outlines in surface view (Figs. 43, 45, 46).The cells are thick-walled and strongly cutinized. Stomata are present only on the lower surface (Figs.

44, 45). They have the outer and inner cuticular ridges strongly developed, so that the front and back cavities are well-formed. The mesophyll consists of two layers of palisade cells separated by a middle layer of cells from the spongy tissue of more or less irregular-shaped cells, which show a tendency to elongate palisade fashion, *i.e.* in the vertical direction. The vascular bundles are enclosed in sclerenchymatous sheaths which in the case of larger bundles, extend from epidermis to epidermis. The structure of the leaf is xeromorphic.

Terminalia Catappa Linn.

It is a large handsome tree with branches in horizontal whorls and leaves which turn red before falling in the hot season. The plant grows in tropical India and Burma (51). It is commonly cultivated in the Bombay Presidency.

The Leaf :

(*A*) *External Features.*—Leaves alternate, clustered towards the ends of branches, very short petioled, obovate from a cordate but very narrow base 15–25 cm., deciduous in the cold season, usually softly hairy when young, hairy or glabrous when adult (3).

(*B*) *Internal Structure.*—(Figs. 47-51). The upper epidermis (Figs. 48, 50) consists of tabular cells with more or less wavy outline when viewed from the surface. The epidermal cells are thick-walled with the lumina often considerably reduced and strongly cutinized. The lower epidermis is less thick-walled. The hairy covering on the lower surface consists of thick-walled unicellular hairs with the lumina of the basal portions enlarged and continued into the distal portions in the form of canals (Fig. 47). Stomata occur only on the lower surface (Fig. 51) being 190 per 1 sq. mm., They are not sunken but the guard cells are extremely thick-walled with narrow lumina and with the front and back cavities well formed by distinct cutinized ridges (Fig. 49). The palisade is made up of two layers of cells, the spongy parenchyma of loosely arranged irregular-shaped cells. The present writers have not had the opportunity to study the vascular system of the leaf. He presumes it is not unlike what Solereder (47) on the authority of Heiden (23) describes for species of *Terminalia* among other genera. He says that "The vascular bundles of the smaller veins are either embedded...or vertically transcurrent. Sclerenchyma accompanies them in large or small amount...In vertically transcurrent veins sclerenchyma...or thin-walled strengthening tissue...extends from the vascular system to the epidermis of each surface." The structure of the leaf is xeromorphic.

Terminalia belerica Roxb.

It is a large deciduous tree with leaves clustered at the ends of branches. In north India leaves even fall in November, the tree being leafless by the end of that month ; while in other parts it may be in full leaf till the end of January. The tree remains leafless until March and May. New foliage appears in May. Flowers appear in April–May (51). The tree is common in the mixed monsoon forests throughout the Presidency (49).
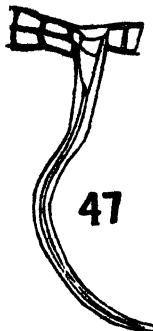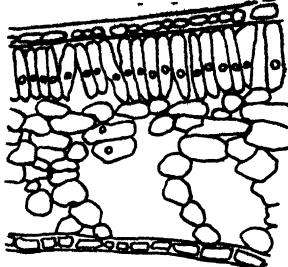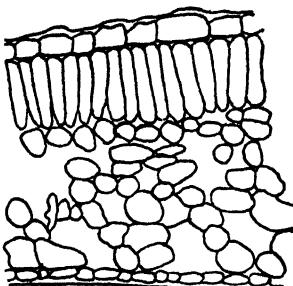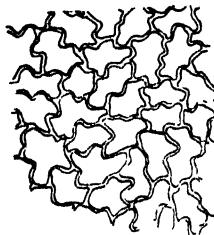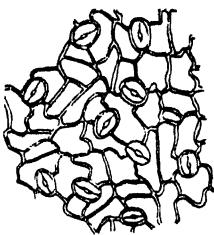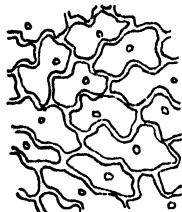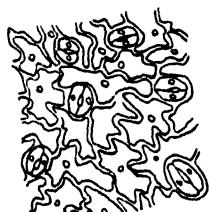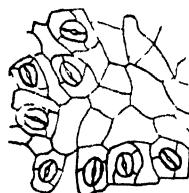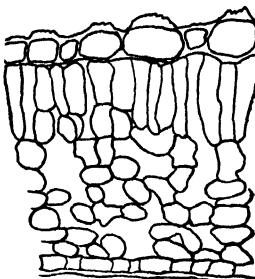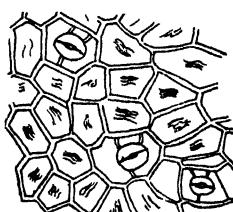
Figs. 47–51.—*Terminalia Catappa* Linn.: Fig. 47. A hair. (× 240); Fig. 48. T. S. of the leaf. (× 240); Fig. 49. Stoma in V S. (× 540); Fig. 50. Upper epidermis (surface view). (× 240); Fig. 51. Lower epidermis (surface view). (× 240).

Figs. 52–55.—*Terminalia belerica* Roxb.: Fig. 52. T. S. of the leaf (× 240); Fig. 53. Upper epidermis (surface view). (× 240); Fig. 54. Lower epidermis (surface view). (× 240); Fig. 55. Stoma in V. S. (× 540).

Figs. 56–59.—*Careya arborea* Roxb.: Fig. 56. T. S. of leaf. (× 240); Fig. 57. Lower epidermis (surface view). (× 240); Fig. 58. A portion of the lower epidermis (surface view) showing the thickness of the lateral cell walls and striations. (× 240); Fig. 59. Upper epidermis (surface view). (× 240).

N B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

The Leaf :

(*A*) *External Features.*—Leaves collected about the extremities of branches, alternate, coriaceous, 4–8 by 3-6 ins., broadly elliptic or elliptic-obovate, rounded or rarely subacute or shortly acuminate at the apex, both surfaces puberulous when young, glabrous and reticulate when old, the margins entire, pellucid, base narrowed (10).

(*B*) *Internal Structure.*—(Figs. 52–55). The structure of the leaf is very similar to that of the leaf of *T. Catappa* described above. The number of stomata on the lower surface is 160 per 1 sq. mm. The structure is xeromorphic.

Careya arborea Roxb.

This tree occurs throughout the Bombay Presidency in deciduous forests. It is a middle-sized or sometimes a large tree attaining 60 ft. with a rounded head (10).

The Leaf :

(*A*) *External Features.*—Leaves alternate, crowded at the ends of branches, 6 12 by 3-7 ins. usually sessile, broadly obovate or oblong-obovate, rounded or shortly acuminate, crenate-denticulate, glabrous, tapering at the base (10).

(*B*) *Internal Structure.*—(Figs. 56–59). The upper epidermis consists of tabular cells (Figs. 56, 57) which in surface view appear more or less polygonal with somewhat straight walls. In transverse section the cells appear barrel-shaped owing to the bulging out of the outer and inner walls. The cell walls are thickened, the thickening being greatest at the crest of the outer walls where also cuticular teeth-like ridges (Fig. 56) may be seen projecting outward. These teeth-like cuticular ridges in the surface view appear in the form of more or less wavy striations running across the middle of the cells (Fig. 58). The lower epidermis consists of smaller cells than the upper epidermis. The cell-walls are also thickened and cutinized, and cuticular ridges may also project from the middle of the outer walls of the cells (Fig. 59). Stomata (Figs. 57, 59) occur on both the surfaces being more numerous on the lower than on the upper. The guard-cells are small and thick-walled, and cuticular ridges are well developed. They are slightly depressed. The mesophyll (Fig. 56) consists of a palisade of one or two layers of elongated cells. Spongy parenchyma is made up of loose irregular-shaped cells with large intercellular spaces. The vascular bundles are fortified by sclerenchymatous sheaths which may surround them completely or may strengthen only the upper and the lower faces. Elongated sclerides occur in the mesophyll. Also water-storing reticulated tracheides are found in the mesophyll. Possibly the thickened outer walls act like concavo-convex lenses with a high refractive index, and have the effect of concentrating light on to the mesophyll (18). The leaf structure is xeromorphic.

Tectona grandis Linn.

The familiar teak tree occurs in the Bombay Presidency in mixed deciduous forests. It is also known to occur in the evergreen forests. Where it does so, it indicates the recent encroachment of evergreen species in former forests of deciduous type (51). Teak usually occurs in dry localities where it is subject to great heat and drought in hot seasons, *e.g.* in places like Khandesh and Ahmednagar where the rainfall is 30 inches or even less, but it reaches its highest development in a moist, warm, tropical climate where the rainfall ranges from 50 to 150 inches. The extent of its deciduousness seems to depend upon the climate, chiefly rainfall. In dry and hot situations and seasons the leaf fall takes place in November, December and January, whilst in moist localities the tree remains in leaf till March or even later. As a rule the trees are bare of leaves for a greater part of the hot season. New foliage usually makes its appearance from April to June (8).

The Leaf :

(*A*) *External Features.*—The leaves are simple ; very large, being 1–2 ft. long and up to about 1 ft. wide. They are much larger in seedlings. In shape, they are elliptic or obovate, acute or acuminate with a cuneate base and entire margin and having the upper surface rough but usually glabrous and the lower surface clothed with dense stellate grey or tawny tomentum. The main nerves are 8–10 pairs with 2 to 3 large branches near the edge of the leaf, joined by numerous parallel transverse veins (10). The latter enclose a closely knitted network of finer veins.

(*B*) *Internal Structure.*—(Figs. 60–77). The transverse section of the leaf has a very undulated outline. Depressions or pits on the under surface correspond to the corresponding projections of the upper surface which appears hammocky (Figs. 60, 61, 62). Each area of depression and its corresponding hammock is actually an areole, *i.e.* a definite area bounded by veins—in other words a vein-islet which represents a well-defined photosynthetic unit. These vein-islets are not all of the same size (Fig. 61) with the result that the depressions on the lower surface and the corresponding projections (hammocks) on the upper surface also vary in size. The cells of the upper epidermis are not tabular (Figs. 64, 65) as ordinary epidermal cells are. They are papillose and show a tendency to elongate vertically as we go from the base to the crest of each hammock. Some of them even elongate into conical projections sufficiently pronounced to be considered hairs. All the cells are strongly cutinized especially on the outer side (Figs. 64, 65). On account of this, as well as due to the unevenness of the surface caused by some cells projecting beyond others, the upper surface has a very rough feel. Such an epidermis functions as water-proof covering, protecting the leaf against excessive transpiration and also as a hard exoskeleton serving to maintain the rigidity of the leaf. The papillose epidermal cells with their thickened outer walls probably have a function similar to that attributed to cells of like shape by Haberlandt (18), *viz.* they act as condensing lenses concentrating the rays of light on to the photosynthetic tissue beneath. Barring these papillose cells whose pro-

PLATE VI

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mesophyll as in Fig 64
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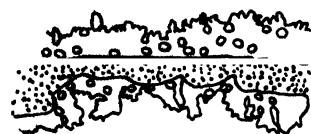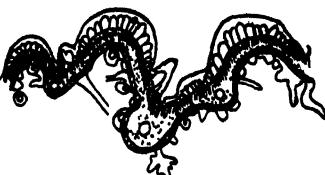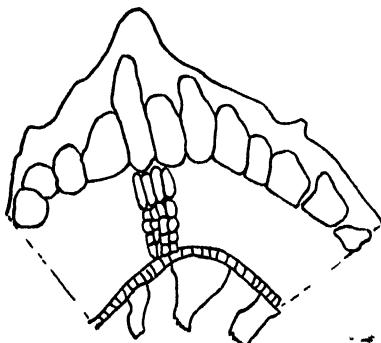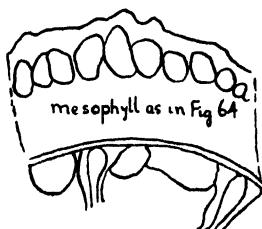
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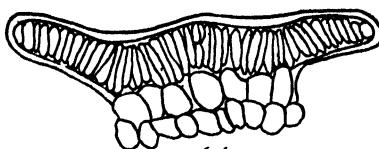
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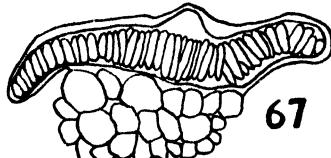
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Figs. 60–67.—*Tectona grandis* Linn : Fig. 60. Semidiagrammatic T. S. of a young leaf showing the hairs on both surfaces crowded together into indistinguishable masses. (× 80); Fig. 61. Semidiagrammatic T. S. of middle-aged leaf (× 80); Fig. 62. Semidiagrammatic T. S. of old leaf. (× 80); Fig. 63 T. S. of young leaf showing the hairs on the upper and lower surfaces magnified : a, glandular hairs ; b, clothing hairs. (× 240); Fig. 64. T. S. of middle-aged leaf. (× 240); Fig. 65. T. S. of old leaf. (× 240); Figs. 66 & 67. Flattened disc-shaped glandular hairs. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

jecting tips render the surface rough and make it feel hairy, the upper
side of the old leaf is, for the most part, glabrous. But this is not the
case with the very young leaf which has a dense tomentum consisting of
branched clothing candelabra hairs (Fig. 63, *b*) and stalked glandular
hairs (Fig. 63, *g*) which latter are specially referred to later. As the
leaf grows the hairs become spaced out, the branched hairs elongating
in all directions, and ultimately, as the need for them as a protective
device becomes dispensed with, owing to the epidermal cells becoming
thickened and cutinized, they are wiped off. The upper epidermis is
devoid of stomata. The epidermis on the lower surface is composed of
tabular cells (Fig 64) which are rather thick-walled on the projecting
portions of the ridges and thin-walled in the depressions. There are no
stomata on the ridges. But interspersed among the epidermal cells
lining the depressions are extremely small stomata (Fig. 71). The
depressions of the teak are comparable to the stomatal chambers on the
under side of the leaf of *Nerium odorum* Soland (13) but whereas the
stomatal chambers of *Nerium* are depressions of the under surface dipping
into the mesophyll, those of *Tectona* do not so dip into the mesophyll but
simply follow corresponding projections (hammocks) of the upper
surface. On the under side, more especially in the depressions, is a
thick coating of clothing hairs intermixed with glandular hairs. The
clothing hairs may be either simple, unbranched, unicellular or multi-
cellular (Figs. 75, 76, 77) ; or they may be much branched candelabra
hairs (Figs. 72, 73, 74). The hairs are more thick-walled in older than
in the younger leaves. They are more numerous and closely matted
together in the depressions where, by reason of the dead air-space
that they form, they constitute an efficient protection against excessive
transpiration. The glandular hairs (Figs. 66–70) are of two types,
both being stalked : In one type the head consists of a few cells forming
a globular structure and depositing its secretion in a sac or cavity formed
between these cells and the cuticle, which separates off from them (Figs.
68–70). In the other type the head is more enlarged breadthwise,
with the secreting elements arranged in the form of a flattened disc
(Fig. 66). In this case also the secretion is collected under the cuticle
that separates off from the cells (Fig. 67). The hairs of the first type
have been referred to by Troup (51) "as minute glandular dots which
are red in young leaves, afterwards turning black." Sections of alcohol
preserved material become stained pink on account of the secretions of
these hairs. The red pigment referred to by Haines (19) probably
comes out of these glandular hairs ; and it appears that the dyeing pro-
perties of the leaves referred to and recommended by Kurz (30) for
dyeing silk yellow, olive, etc., is due to the pigment secreted by these
glandular hairs. The photosynethetic tissue (Fig. 64) is typically
xeromorphic. The palisade tissue consists of one layer of cells which
are about three times as long as broad and closley packed. The spongy
tissue is made up of four to five layers of isodiametric cells closely packed
together with scarcely any air-spaces. The vascular tissue of the leaf
forms an anastomosing network. There are large areoles enclosing
smaller areoles, but all so perfectly arranged as to give the general effect
of the rigidity that is necessary to support such a large leaf surface.
The closely knitted venation further ensures perfect circulation of fluids
(18), and also, in the writers, opinion, brings about the complete isolation

of the photosynthetic units into water-tight compartments, so that in case of accidental injury or damage caused by insects to any of the units, there is no danger of dessication to the rest of the leaf. The structure of the leaf is strikingly xeromorphic.

Gmelina arborea Roxb. '

It is a moderate-sized, unarmed, deciduous tree, reaching 60 ft. high (10).

The Leaf:

(*A*) *External Features.*—The leaves are 4-8 ins. by 3-6 ins., broadly ovate, acuminate, entirely glabrous above when mature, stellately fulvous-tomentose beneath, base cordate or sometimes truncate and shortly cuneate (10).

(*B*) *Internal Structure.*—(Figs. 78-80). The upper epidermis consists of tabular cells (Fig. 78) with more or less irregular outlines in surface view (Fig. 80). The outer walls are extremely thick and strongly cutinized. There are no stomata. The upper epidermal surface is straight in section while the lower epidermis is undulated, there being convexities and concavities on the under side (Fig. 78). Epidermal hairs occur on the lower side. They are of two types, *viz.* (*a*) capitate hairs consisting of a short stalk-cell and a two-celled or a two-rayed head (Figs. 78, 79) and (*b*) long uniseriate trichomes of thick-walled cells made up of a short basal cell and a limb consisting of two or more terminal elongated cells with a canal running through the length of each cell (Fig. 81). The short stalked capitate hairs form a close tomentum which protects the lower epidermis and screens the stomata. The latter (stomata) being sufficiently protected by the hairs, are not depressed, but are somewhat raised structures with the outer cuticular ridges prominently developed (Fig. 79). In the region of the mid-rib and main veins the epidermal cells, both upper and lower, are thick-walled, strongly cutinized and convexly arched. The palisade is made up of one to two layers of elongated cells. The spongy parenchyma consists of irregular-shaped more or less isodiametric cells (Fig. 78). The leaf structure is xeromorphic.

Euphorbia neriifolia Linn. (=*E. ligularia* Roxb.)

This is an erect fleshy glabrous shrub or a small tree seldom reaching 20 ft. high, branches scattered, ascending, the young ones 5-sided, angled, with short stipular sharp spines arising from thick tubercles, arranged in 5 irregular rows (10). The plant is a typical xerophyte. The stems are all green phylloclades, and for the greater part of the year the plant is bare of leaves. The leaves last only during the rains. Old leaves are shed before September. Young leaves appear in April-May only in localities with fairly abundant rainfall, and in dry places. The plant occurs throughout the dry Deccan common in open thorn forest formations in Poona, Satara and Nasik Districts, and also on the Ghats under heavy rainfall (49). It is often planted as a fence (10).

PLATE VII
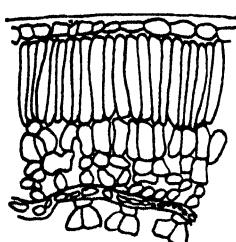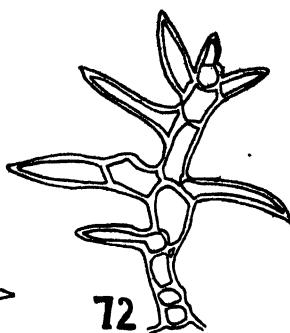
Figs. 68–77.—*Tectona grandis* Linn.: Figs. 68–70. Small glandular hairs (× 240); Fig. 71. Stoma. (× 720); Figs. 72 & 77. Hairs from old leaf. (× 240); Figs. 73, 75 & 76. Hairs from middle-aged leaf. (× 240); Fig. 74. A hair from young leaf. (× 240).

Figs. 78–81. *Gmelina arborea* Roxb: Fig. 78. T. S. of leaf. (× 240); Fig 79 Portion of T. S. of the lower epidermis showing stomata. (× 240); Fig. 80 Upper epidermis (surface view). (× 240); Fig. 81. A hair. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

The Leaf :

(A) *External Features.*—Leaves 6–12 by 2–3 ins., alternate, near the tops of branches, obovate-oblong. or subspathulately obovate, acute, deciduous, base narrowed into a very short petiole (10). Stipules transformed into spines. The leaf-blades are tender, fleshy, more or less light green above, and pale beneath.

(B) *Internal Structure.*—(Figs. 82–87). The upper and lower epidermal cells are tabular (Figs. 82, 85, 86) with more or less straight outlines when viewed from the surface (Figs. 84, 87). The cells of the epidermis are moderately thickened and slightly cutinized. Stomata occur on both surfaces (Figs. 84, 85, 86, 87). The stomatal frequency is 40 and 128 per 1 sq.mm. for the upper and lower epidermis respectively. The mesophyll (Figs. 82, 83, 85, 86) is bifacial. The palisade cells are short and disposed in 3–5 layers. The spongy parenchyma is made up of isodiametric more or less rounded or oval cells with large air-spaces. The vascular tissue is poorly developed, and the mechanical tissue feeble. The leaf thus has a mesophytic structure. As it is required to function only under moist monsoon conditions, its mesophytic structure is easily understood. The plant is the only one of the group of deciduous trees and shrubs dealt with in this work which, unlike the others described herein, has leaves corresponding in texture and structure to the leaves of deciduous plants of temperate regions, *viz.* they are mesophytic (52).

Bridelia retusa Spr.

Bridelia retusa Spr. is a moderate-sized deciduous tree, spinous when young (10).

The Leaf :

(A) *External Features.*—Leaves alternate, simple, usually quite entire, 3–6 by 1½–2½ ins., rigidly coriaceous, elliptic-oblong, obtuse, subacute or rounded at the apex, with entire or slightly crenulate margins, bright green and glabrous above (turning pinkish-brown before falling), glaucuous and usually finely tomentose beneath, base usually rounded (rarely cordate) ; main nerves prominent, straight, 15- 25 pairs with finely reticulate venation between (10).

(B) *Internal Structure.*— (Figs. 88–92). The anatomy of *Bridelia stipularis* Bl. has been investigated by Solereder (47), but so far *Bridelia retusa* Spr. has not been done. In the transverse section the upper side shows a straight outline without any depressions but the lower side has deep concavities and convexities (Figs. 88, 91). The convexities correspond to the ridges and are due to the position of vascular bundles. The depressions furnish so many outer chambers for the stomata which are situated in the epidermis that lines them (Figs. 88, 90). The upper epidermis (Figs. 88, 89) is made up of large more or less tabular cells having more or less straight outlines in surface view. It is thick-walled especially on the outer side and strongly cutinized. The lower epidermal cells show a tendency to grow outwards and elongate in the form of papillae (Figs. 88, 90). The elongation is much more pronounced in the depressions than on the ridges, and in the former case, they serve

PLATE VIII

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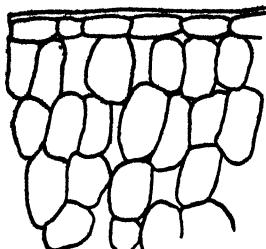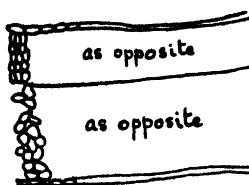
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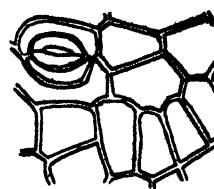
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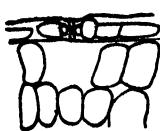
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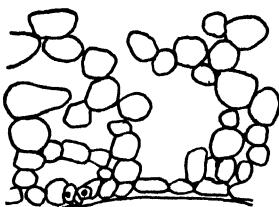
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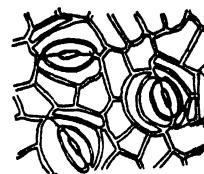
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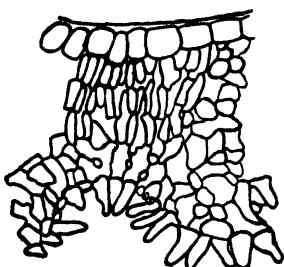
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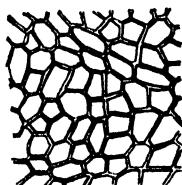
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Figs. 82–87.—*Euphorbia neriifolia* Roxb.: Fig. 82. Portion of the upper epidermis and palisade tissue in T. S. (× 240); Fig. 83. T S. of leaf (semi-diagrammatic). (× 80); Fig. 84. Upper epidermis (surface view). (× 240); Fig. 85. A portion of leaf in T. S. showing stoma on the upper side. (× 240); Fig. 86. A portion of leaf in T.S. showing stoma on the lower side. (× 240); Fig. 87. Lower epidermis (surface view). (× 240).

Figs. 88–92.—*Bridelia retusa* Spr: Fig. 88. T. S. of leaf. (× 240); Fig. 89 Upper epidermis (surface view). (× 240); Fig. 90. A portion of the T. S. of leaf showing stoma on the lower side. (× 240); Fig. 91. T. S. of leaf showing the depressions on the under side of the leaf (diagrammatic.) (× 80); Fig. 92. A hair. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

to screen the stomata which are found distributed among the epidermal cells lining the depressions. Such papillose epidermal cells have been recorded for a number of *Euphorbiaceae* (47). Further protection to the stomata is afforded by multicellular piotecting hairs which occur mostly on the veins and stretch across horizontally overarching the depressions and forming a sort of a loose roof or thatching over the depressions as in the case of *Semecarpus Anacardium* described above. The stomata which are situated amongst the bases of the epidermal papilla, show no special xerophytic features as they are sufficiently protected by their position in the depressions and by the hairs lining these depressions. The mesophyll (Fig. 88) is made up of about three to four compact layers of palisade cells and spongy parenchyma consisting of loosely arranged irregular-shaped cells. The lower cells of the spongy parenchyma have brown contents. The vascular bundles are enclosed in sheaths which in the case of the larger veins extend from epidermis to epidermis and are often fortified by sclerenchymatous strands occurring on the upper and the lower faces of the vascular bundles. The cells of the sheaths are also found to have brown contents. The structure of the leaf is xeromorphic.

Jatropha Curcas Linn.

This plant is a native of tropical America, commonly grown as a fence near villages (10). Though Hooker (24) says that the plant is evergreen it does not appear to be so always. In extreme dry weather it sheds its leaves.

The Leaf :

(A) *External Features.*—Leaves scattered on the older branches; closely packed at the top of the youngest branches; the youngest leaves of a reddish tinge, with a tomentose under surface, the tomentum disappearing as the leaf grows old and assumes a green colour. Upper surface smooth. Shape broad-cordate, or orbicular-cordate; 5-angled. Leaves 3-5 lobed, 4-6 ins. long (10, 26).

(B) *Internal Structure.*—(Figs. 93-97). The structure of the leaf is bifacial (Fig. 93). The upper epidermal cells are much larger than the lower and are more strongly thickened and cutinized. The epidermal cells are tabular and appear more or less polygonal with straight outlines in surface view (Figs. 94, 95). In the upper epidermal cells are observed some crystalline aggregates resembling in structure inulin crystals. Stomata are found on both the surfaces. They have prominent cuticular ridges. They project above the surface on the lower side (Fig. 96) but on the upper side (Fig. 97) they are slightly depressed. The palisade tissue consists of two to three layers of elongated cells. The spongy parenchyma is made up of small irregular-shaped cells. In the mesophyll are distributed cells containing clustered crystals (S in Fig. 93). The palisade cells have very often dark contents, so too the cells of the spongy parenchyma towards the lower side. Storage tracheides (t in Fig. 93) occur in the mesophyll. The structure is xeromorphic.

2. Evergreen Trees and Shrubs

Anacardium occidentale Linn.

This is a tropical evergreen tree possessing glabrous thickly coriaceous leaves. It is a native of South America and has become naturalized in many places in India. It is often gregarious and thrives best in sandy places and is important in reclamations of sand dunes (51). In the Bombay Presidency it occurs in Bombay Island, Salsette and in the Konkan (10).

The Leaf:

(A) *External Features.*—The leaves are alternate, exstipulate, simple, quite entire and coriaceous, 4-6 by 2½-3 ins., obovate or elliptic, rounded at the apex, glabrous, finely reticulately veined, base cuneate ; main nerves 10-12 pairs, prominent beneath (10).

(B) *Internal Structure.*—(Figs. 98 –106). Although a good deal of work has been done on the stem anatomy of the *Anacardiaceae* and the genus *Anacardium* has also received attention in this respect (47), very little information is available regarding its leaf structure. The upper as well as the lower epidermis are made up of tabular cells with wavy outlines, having extremely thickened stratified and strongly cutinized cell walls (Figs. 98, 99, 100). The side and inner walls of the cells are pitted (Figs. 105, 106) and the outer walls bear striations caused by projecting cuticular ridges. There is a coating of waxy granules (Figs. 99, 100) over the cuticle which is more abundant on the lower side. The stomata (Figs. 103, 104) occur only on the under side. They are not sunken but the guard-cells have very thick and strongly cutinized walls with narrow lumina. Cubical crystals occur in the epidermal cells both of the upper and lower sides. The mesophyll is bifacial. It consists of two layers of palisade cells, and a spongy parenchyma of irregular-shaped more or less isodiametric cells somewhat loosely arranged. Secretory ducts (Fig. 102) occur in the mesophyll and also in the vascular bundles. In the latter they occupy the position of the phloem. The veins are strongly supported by sclerenchyma (Fig. 101) which, in the case of larger veins extends from epidermis to epidermis and in conjunction with the thick-walled and strongly cutinized epidermis, which acts as a hard exoskeleton, forms an efficient mechanical tissue, making for the rigidity of the leaf. The thick-walled, cutinized epidermis also serves as a waterproof covering to the leaf. The leaf is xeromorphic.

Ixora coccinea Linn.

This is a glabrous, evergreen shrub, about 2-3 ft. high, common in Salsette and in the Konkan and indigenous in the Bombay Presidency (10).

The Leaf:

(A) *External Features.*—The leaves are simple, opposite with interpetiolar stipules, having a long rigid cuspidate point. They are coriaceous, pale when dry, sessile or nearly so, oblong, obtuse (rarely acute)-apiculate, base rounded or sub-cordate ; main nerves 8-12 pairs, slender (10).

PLATE IX
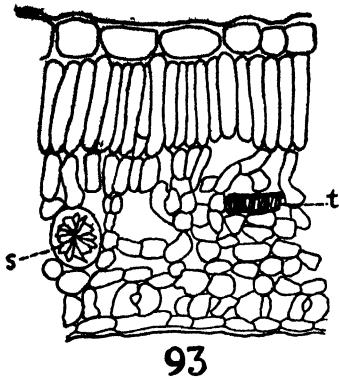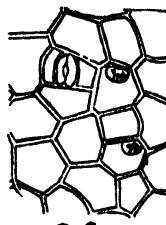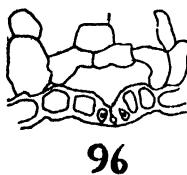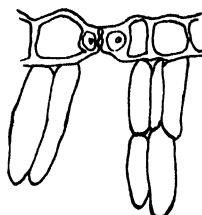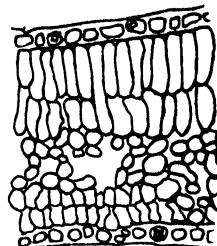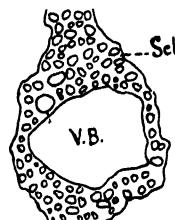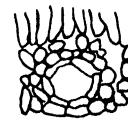
Figs. 93–97.—*Jatropha Curcas* Linn.: Fig 93. T. S. of leaf: *t*, tracheides; *s* crystals. (× 240); Fig. 94. Upper epidermis (surface view). (× 240); Fig. 95. Lower epidermis (surface view). (× 240); Fig. 96. Portion of T. S. of leaf showing a stoma on the under side. (× 540); Fig. 97. Portion of T. S. of leaf showing stoma on the upper surface. (× 540).

Figs. 98–106.—*Anacardium occidentale* Linn: Fig. 98. T. S. of leaf. (× 240); Fig. 99. Upper epidermis in T. S. showing the thickening of walls and granules (*gr*). (× 720); Fig. 100. Lower epidermis in T. S. showing the thickening of walls and granules(*gr*). (× 720); Fig. 101. Vascular bundle (*V.B.*) with a portion of sclerenchymatous sheath (*Scl*). (diagrammatic). (× 240); Fig. 102. Duct. (× 240); Fig. 103. Stoma in V. S. (× 540); Fig. 104. Stoma in surface view. (× 540); Fig. 105. Upper epidermis (surface view). (× 540); Fig. 106. Lower epidermis (surface view). (× 540).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

(B) Internal Structure.—(Figs. 107-110). Our knowledge of the structure of the leaf of the *Rubiaceae* is still very insufficient (47). In *Ixora coccinea* Linn. the upper and the lower epidermis consist of cells which appear more or less squarish or tabular in transverse section (Fig. 107). Both are strongly thick-walled and cutinized especially the outer walls. In surface view (Figs. 109, 110) they appear more or less polygonal, and on the lower side, show striations due to outwardly pro-jecting cuticular ridges. The stomata (Fig. 108) are not sunken but the guard-cells are extremely thick-walled so that their lumina are almost obliterated. They are also provided with strong cuticular ridges marking off definite back and front cavities. The mesophyll cells—both palisade and spongy—are also thick-walled. The palisade tissue consists of two to three layers of elongated compactly arranged cells. The spongy parenchyma is composed of isodiametric cells also compactly arranged with few and smaller air-spaces. All the cells of the mesophyll contain a brown pigment (tannin). The vascular bundles appear embedded and the sheaths enclosing them do not extend to the upper and lower epidermis. The need for this is dispensed with by the compact character of the mesophyll tissue whose cells also, together with those of the epider-mis, are considerably thick-walled and provide adequate mechanical support to the leaf. The internal protection afforded by the thickening and cutinization of the walls of the mesophyll cells also accounts for the stomata not being sunken. The leaf is typically xeromorphic.

Mimusops Elengi Linn.

It is a large evergreen tree, 40–50 ft. high, with a compact leafy head and short erect trunk. It occurs in the ravines in the Ghats, in the evergreen forests of the Konkan at Matheran and in the evergreen forests of North Kanara (10).

The Leaf :

(A) *External Features.*—Leaves 2½–4 by 1½–2 ins., elliptic, shortly acuminate, glabrous, base acute or rounded (10).

(B) *Internal Structure.*—(Figs. 111-114). There is an upper epider-mis of two layers of more or less tabular cells with irregular (not wavy) outline as seen in surface view (Figs. 111, 112). The lower epidermis is one- or two-layered (Fig. 111). Epidermal cells have thick walls very strongly cutinized. Stomata are present only on the under side (Figs. 113, 114). Their guard-cells lie level with the epidermal cells and have extremely thick walls with reduced lumina and strong cuticular ridges. The palisade tissue consists of two layers of elongated cells and a spongy parenchyma of loosely arranged isodiametric cells (Fig. 111). Situated in the mesophyll is a large number of branched sclerides (thick-walled sclerotic cells) extending from epidermis to epidermis. These sclerides obviously act as mechanical supports propping up the firm epidermis and giving the leaf a remarkable firmness. The vascular bundles are embedded in sheaths of sclerenchymatous cells which in the case of the larger veins also extend from epidermis to epidermis and act as I-girders. The branched sclerides and the I-girders have the combined effect of counteracting the loss of firmness occasioned by the loosely arranged spongy parenchyma. The structure is xeromorphic.

PLATE X

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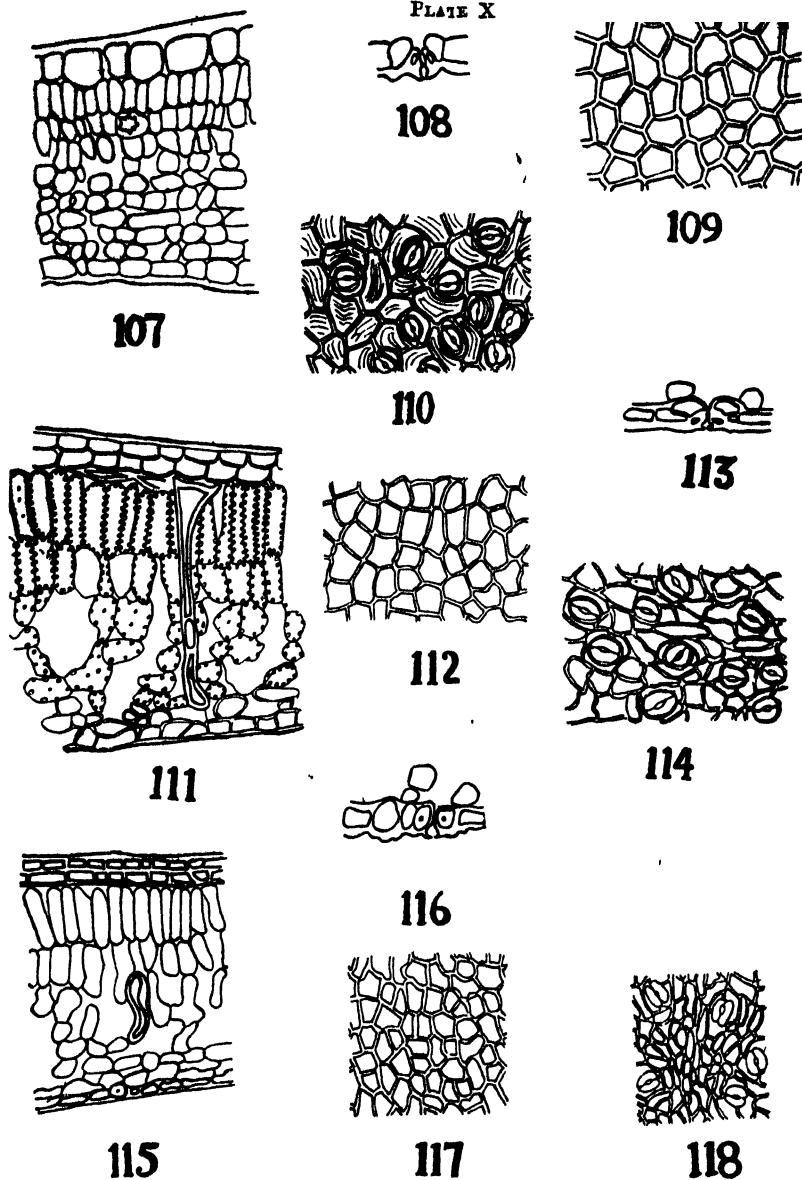
Figs. 107–110.—*Ixora coccinea* Linn.   Fig. 107. T. S. of leaf. (× 240); Fig. 108.
Stoma in V. S. (× 540); Fig. 109. Upper epidermis (surface view) (× 240); Fig. 110
Lower epidermis (surface view). (× 240).

Figs. 111–114.—*Mimusops Elengi* Linn : Fig. 111. T. S. of leaf. (× 240);
Fig. 112. Upper epidermis (surface view). (× 240); Fig. 113. Stoma in V. S. (×
540); Fig. 114. Lower epidermis in surface view. (× 240).

Figs. 115–118.—*Mimusops hexandra* Roxb: Fig. 115. T.S. of leaf. (× 240); Fig. 116.
Stoma in V. S (× 540); Fig. 117. Upper epidermis (surface view). (× 240); Fig. 118.
Lower epidermis (surface view). (× 240).

  N.B.—The figures have been reduced in reproduction. To get the initial magnifi-
cation indicated after each figure multiply by 2.1.

Mimusops hexandra Roxb.

It is a large evergreen tree, 50–60 ft. high, with a shady head ; trunk erect without branches for a considerable height. It grows in the dry forests of the Deccan, Khandesh and Gujarat (10).

The Leaf :

(A) *External Features.*—Leaves coriaceous, 2–4½ by 1–2 ins., obovate or oblong, rounded or emarginate at the apex, glabrous on both sides, dark green and polished above, paler beneath, base acute (10).

(B) *Internal Structure.*—(Figs. 115–118). The upper epidermis (Figs. 115, 117) is made up of two layers of tabular cells which appear more or less irregular in outline with somewhat straight walls (not wavy). The cell walls of the epidermis are strongly thickened and cutinized (Fig. 115). Stomata are absent from the upper epidermis. The lower epidermis (Figs. 115, 118) is also two-layered and considerably thickened and cutinized. The stomata are thick-walled and cutinized with strong cuticular ridges (Fig. 116). The mesophyll consists of a compact palisade of two layers of cells and a spongy parenchyma made up of more or less loosely arranged isodiametric irregular-shaped cells. Arm sclerides occur but in smaller number than in *Mimusops Elengi.* The structure is xeromorphic.

Marsdenia volubilis Cooke

It is a large twining shrub, not uncommon in the Bombay Presidency. *The Leaf :*

(A) *External Features.*—Leaves 2½–6 by 1¾–4½ ins., broadly ovate or orbicular, acuminate, glabrous or more or less softly pubescent, reticulately veined and with a few small glands just above the petiole (10).

(B) *Internal Structure.*—(Figs. 119–122). Unlike the leaf of *Marsdenia erecta* which has a centric structure (47) the leaf of *Marsdenia volubilis* Cooke is bifacial (Fig. 119). The epidermis as in other xerophilous species of the family (47) consists of thick-walled tabular cells considerably cutinized especially on the outer side (Figs. 119, 120). There is an excretion of wax on the surface. The epidermal cells appear polygonal with straight walls in surface view (Figs. 121, 122). Stomata (Figs. 120, 122) occur only on the lower side. The guard cells are sunken below the general surface of the epidermis and are thickened so that the lumina are considerably reduced. They are provided with strong cuticular ridges. The mesophyll consists of a single layer of palisade cells and a considerable spongy parenchyma of irregular-shaped somewhat isodiametric cells with abundant air-spaces. The structure is xeromorphic.

Argyreia speciosa Sweet

It is a very large climber, a doubtful native of the Bombay Presidency, It is cultivated throughout India and, in the Bombay Presidency, it is found chiefly near villages (10).

The Leaf :

(A) *External Features.*—Leaves 3–11 by 2½–10 ins. (sometimes even larger) ovate, acute, glabrous above, persistently white-tomentose beneath, base cordate (10).

PLATE XI
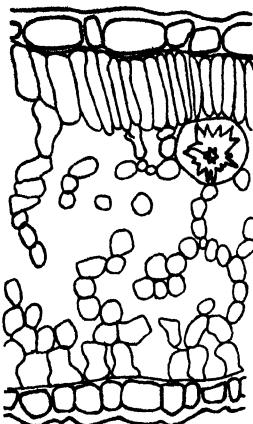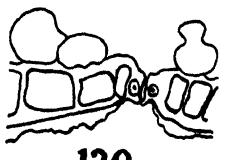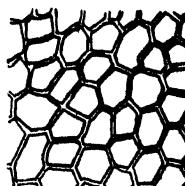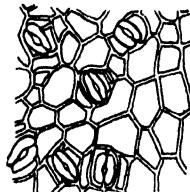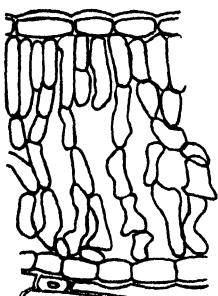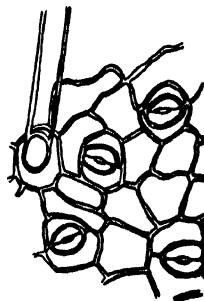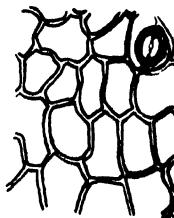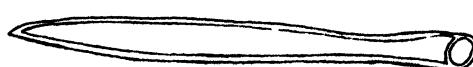
Figs. 119–122.—*Marsdenia volubilis* Cooke : Fig. 119. T. S. of leaf. (×240); Fig. 120. Stoma in V. S. (× 540); Fig. 121 Upper epidermis (surface view). (× 240); Fig. 122. Lower epidermis (surface view). (× 240).

Figs. 123–127.—*Argyreia speciosa* Sweet : Fig. 123. T. S. of leaf. (× 240); Fig. 124. Stoma in V. S. (× 540); Fig. 125. Lower epidermis (surface view). (× 240); Fig. 126. Upper epidermis (surface view). (× 240); Fig. 127. A hair (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

(*B*) *Internal Structure.*—(Figs. 123-127). The anatomical features of the *Convolvulaceae* have been treated by Hallier (20) chiefly on whom Solereder (47) has based his statements. In *Argyreia speciosa* the upper and the lower epidermis (Figs. 123, 125, 126) consist of tabular cells which appear somewhat polygonal with straight side walls in surface view. The cell-walls especially on the outer side are moderately thickened, those of the upper epidermis more so than those of the lower. Long clothing hairs (Figs. 123, 125, 127) occur on the under surface and consist of a short stalk-cell and an extremely long terminal cell which projects horizontally running parallel to the lower surface. The effect of a large number of such hairs on the underside where the greater number of stomata occur is easily understood. Stomata occur on both the surfaces being 24 and 108 per 1 sq. mm. respectively in the upper and the lower epidermis. They are slightly sunken and are accompanied by subsidiary cells but the cell-walls of the guard-cells are considerably thickened and provided with slight cuticular ridges (Fig. 124). The mesophyll tissue (Fig. 123) consists of two to three layers of palisade cells and a loose spongy parenchyma which is made up of irregular-shaped cells which appear to be elongated more in the vertical direction, the mesophyll thus showing an approach to the isobilateral type. The structure is xeromorphic.

Loranthus longiflorus Desv.

This is one of the commonest stem-parasites on mango trees in Bombay and throughout the Konkan. (10). It is parasitic also on many other kinds of trees, *e.g. Gossampinus malabarica* Merr. The specimen under investigation was growing on *Grewia tiliaefolia* Vahl. The parasite remains evergreen even on deciduous hosts and seems not to be affected by the leaf shedding of the hosts.

The Leaf :

(*A*) *External Features.*—Leaves thick, coriaceous, usually opposite, 3-7 by ¾-4 ins., very variable in shape and venation, ovate, elliptic, or linear–oblong, obtuse ; midrib prominent, usually red, the secondary nerves obscure (10). The leaves usually present their edges to the sky after the manner of phyllodes.

PLATE XII
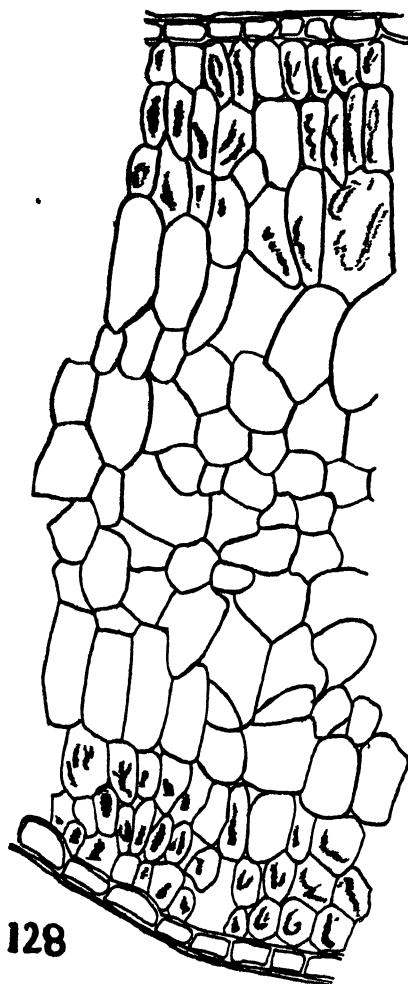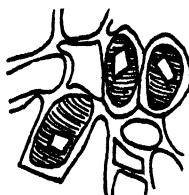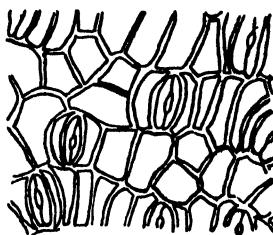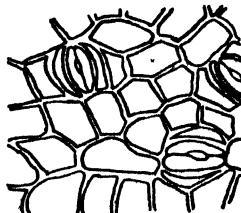
Figs. 128–132.—*Loranthus longiflorus* Desv. : Fig. 128 T. S. of leaf. (× 240); Fig. 129. Mesophyll containing sclerides with solitary crystals. (× 540); Fig. 130. Stoma in V. S. (× 540); Fig. 131. Lower epidermis in surface view. (× 240); Fig. 132. Upper epidermis in surface view. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2₁1.

(B) *Internal Structure.*—(Figs. 128–132). Corresponding to their profile lie, the structure of the leaves is isobilateral (Fig. 128). The epidermis (Figs. 131, 132) is more or less similar on both sides consisting of tabular thick-walled cells with a strongly developed cuticle. In surface view the epidermal cells appear polygonal with more or less straight walls. Stomata occur on both the surfaces and are associated with subsidiary cells. They are almost equally numerous on both sides being about 116 and 120 per 1 sq. mm. in the upper and lower epidermis respectively. The guard-cells (Fig. 130) are small and sunken below the level of the subsidiary cells. The outer cuticular ridges occur in connection with the subsidiary cells so that the external air-chamber is divided into two compartments : (*a*) the outer (*o*) bounded by cuticular ridges projecting from the overlying subsidiary cells and (*b*) the inner (*i*) overarched by cuticular ridges of the guard-cells. The mesophyll consists of more or less uniform cells with well-thickened walls. It is quite compact. The cells that are on the upper and the lower sides of the section are elongated in palisade manner at right angles to the surface. Those in the centre show a tendency to be somewhat isobilateral. About three layers of the mesophyll, just below the epidermis both on the upper and the lower side, contain tannin. In the mesophyll there occur branched thick-walled sclerides containing solitary crystals (Fig. 129). These sclerides occur in connection with the vascular bundles and are also found free in the mesophyll. These structures have been mentioned by Mentovich (35) and Marktanner-Turneretscher (33) as occurring in the tissue of the leaf and in the pith and cortex of *L. europaeus* Jacque and by Solereder (47) in the leaves of *L. ferrugineus* Roxb. and *L. punctatus* R. & P. Marktanner-Turneretscher who discovered the structures regarded them as water-storing mucilage bodies, an interpretation which was found to be erroneous when Ravn Kolpin (27) recognized their siliceous character. The leaf is typically xeromorphic.

Ficus hispida Linn.

This is a shrub or small tree common in many parts of India and Burma usually in shady places (51). In the Bombay Presidency it is found along the banks of rivers and in moist situations (10). It is common in evergreen forests near the sea-coast.

The Leaf :

(A) *External Features.*—Leaves simple, usually opposite, petiolate, membranous, 4–12 by 2–6 ins., ovate, oblong, or subobovate, apiculate or shortly and abruptly acuminate, toothed or entire, the lower surface hispid-pubescent, the upper hispid-scabrid, base rounded, subcordate or subcuneate, 3–5-nerved ; lateral main nerves 3–5 pairs with fine reticulations between (10).

(B) *Internal Structure.*—(Figs. 133—137). The upper epidermis (Figs. 133, 134) consists of tabular cells appearing polygonal with more or less straight outlines in surface view. The cells have extremely thick and strongly cutinized outer walls. Inner walls are relatively less thickened. Distributed among the epidermal cells are smaller cells with crystal contents. Here and there the upper epidermis is two or three-layered with thick-walled cells. Stomata are wanting on the upper surface.

Hairs are also wanting on the upper surface except in very rare instances. When present they are straight, unicellular and extremely thick-walled and verrucose. The lower epidermis (Fig. 136) has relatively small cells, compared to the upper epidermis, and with wavy outlines in surface view. Here and there there are large globular cells (Figs. 133, 136, c) containing cystoliths which are suspended on peg-like projections of the outer cell-walls. The stomatal frequency is 400 per 1 sq. mm. on the lower epidermis. The guard-cells are extremely thick-walled with very narrow lumina and have strongly cutinized ridges forming a conspicuous outer chamber (Fig. 137). Unicellular hairs (Fig. 135) are mostly confined to the veins. They are extremely thick-walled and studded with granular encrustations (verrucose). The thickness of the wall is often so great as to obliterate the lumen in the distal portion of the hair. The mesophyll consists of two to three layers—usually two—of palisade cells which are about two to three times longer than broad. The spongy parenchyma consists of three to four layers with few intercellular spaces. Here and there in the mesophyll are to be found round cells containing crystal aggregates. The vascular bundles are embedded in sheaths of clear cells which in the case of the larger veins extend from epidermis to epidermis and often become sclerenchymatous. The structure is xeromorphic.

Artocarpus integrifolia Linn.

This is a large evergreen tree, glabrous except the youngest shoots. It is said to be indigenous in some of the forests of the Western Ghats. In the Bombay Presidency it is found only in the neighbourhood of villages or near the sites of deserted villages. (10).

The Leaf :

(A) *External Features.*—Leaves 4–8 ins. long, elliptic or obovate, acuminate, entire, or those of the young plants sometimes lobed, dark-green and shining above, rather rough beneath, base narrowed ; main nerves 7–8 pairs (10).

(B) *Internal Structure.*—(Figs. 138–143). The structure of the leaf is characteristic (Fig. 138). The upper epidermis (Figs. 138, 139, 140) consists of tabular cells with wavy outlines in surface view and with very thick strongly cutinized walls. The lower epidermis (Figs. 138, 140, 143) has a similar structure. Stomata are present only on the under side. The mesophyll is strikingly differentiated. The palisade consists of two layers of relatively short compactly arranged cells (Figs. 138, 139). It is very narrow when compared to the spongy parenchyma which is about four times as broad as the palisade tissue. The spongy tissue (Figs. 138, 142) is of a very loose texture, being made up of branched elongated cells which anastomose and form a tissue which appears like a loose network in the transverse section. The photosynthetic areas in the leaf which correspond to the vein-islets are sharply delimited from one another by sheaths (Fig. 138, s) enclosing the vascular bundles. These sheaths extend from epidermis to epidermis and are also fortified by sclerenchymatous fibres. These sheaths therefore not only serve to mark out and isolate the separate photosynthetic areas, but also act as I-girders, which, together with the firm epidermis, keep the structure

PLATE XIII
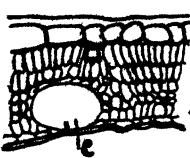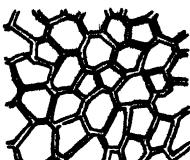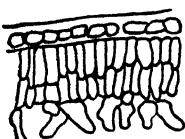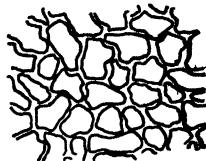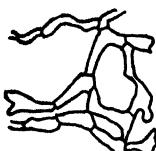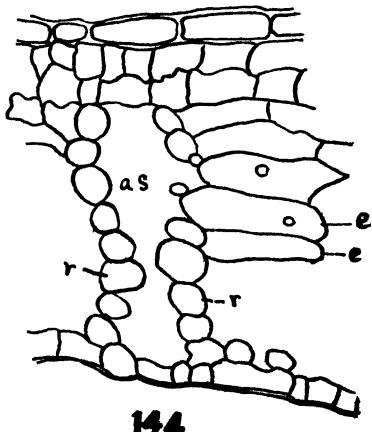
Figs. 133-137.—*Ficus hispida* Linn. : Fig. 133. T. S. of leaf: *c*, cystolith. (×
240) ; Fig. 134. Upper epidermis (surface view) (× 240) ; Fig. 135. A hair. (×240);
Fig. 136. Lower epidermis (surface view). (× 240) ; Fig. 137. Portion of the lower
epidermis in S, showing stoma. (× 720).

Figs. 138-143.—*Artocarpus integrifolia* Linn. : Fig. 138. T. S. of leaf. (diagram-
matic) : *v. b.* Vascular bundle ; *s*, sheath. (× 80) ; Fig. 139. Porton of the upper
epidermis in T. S. with the palisade layer. (× 240) ; Fig. 140. Stoma in V. S. (×240);
Fig. 141. Upper epidermis (surface view). (× 240) ; Fig. 142. Portion of spongy
parenchyma in T. S. (× 240) ; Fig. 143. Lower epidermis (surface view). (× 240).

Fig. 144.—*Smilax macrophylla* Roxb. : T. S of leaf : *a.s.* , air spaces; *r*, rounded
mesophyll cells ; *p*, upper compact mesophyll ; *e*, transversely elon-gated mesophyll
cells. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnifi-
cation indicated after each figure multiply by 2.1.

from collapsing. The importance of the strong I-girders in view of the very loose texture of the mesophyll is obvious. The cells forming the sheaths often contain dark contents, probably tannin. The structure is xeromorphic.

Smilax macrophylla 'Roxb.

It is a large prickly climber, climbing by means of tendrils, common in the Deccan and Konkan and widely distributed in India. In drier districts the plant has been observed to shed its leaves. Young shoots appear before the rains.

The Leaf :

(A) *External Features.*—Leaves alternate, 3–8 by 1½–4½ ins., broadly ovate, or suborbicular, acuminate or cuspidate, glabrous, polished and shining, base usually rounded; main nerves 5–7 (usually 5) with reti-culate venation between (10) ; petioles with two long tendrils above the base.

(B) *Internal Structure.*—(Figs. 144–148). The upper and the lower epidermis (Figs. 144, 147, 148) consist of tabular cells with more or less wavy outlines in surface view. The walls are moderately thickened. The stomata which are present on both sides (being more numerous on the under side) have strong cuticular ridges. The mesophyll (Figs. 144, 145, 146) is composed of uniform cells showing a general tendency to arrange themselves in superimposed tiers and to produce arms hori-zontally from their sides. The arms of adjacent cells of the same tier meet to enclose an air-space (*a. s.*) As the tiers of these enclosing cells are placed one above the other, a vertical passage (as in Fig. 144) is produced, which runs from epidermis to epidermis. In the upper portion of the mesophyll, above the vascular bundles the body of the cells is larger, rendering the air-space narrower, and consequently the mesophyll (*p*) in the upper part appears more compact. In the lower part of the section of the leaf the air-spaces appear expanded, the cells assuming the form of arcs of a circle which meet by their edges. In consequence of this arrangement the cells which are cut in various planes in a transverse section appear : some elongated in a transverse direction (Fig. 144, *e*) and some rounded (Fig. 144, *r*). The former appearance is due to the section having cut the cell more or less along its length as the cell '*a*' in Fig. 146. In the latter case the rounded appearance of the cell is due to the section having cut the cell across as the cells '*b*' and '*c*' in the figure. Such an arrangement of the mesophyll is not without its significance. In the upper part of the leaf, which gets most of the illumination, the mesophyll is more or less compact with small inter-cellular spaces. This part of the mesophyll on account of its position, gets the fullest benefit out of the sunlight. The light that penetrates to the lower portion of the mesophyll is very much weakened and the larger air-spaces surrounded by the arc-shaped cells offer a freer passage for the light which penetrates to the chloroplasts which are arranged along the walls bordering on these air-spaces. Brown contents are found in the upper two layers of the mesophyll and also in the lowermost layer. The vascular bundles are situated between the uppermost compact and the lower loose mesophyll. Horizontally elongated cells containing raphides occur in the mesophyll.

PLATE XIV
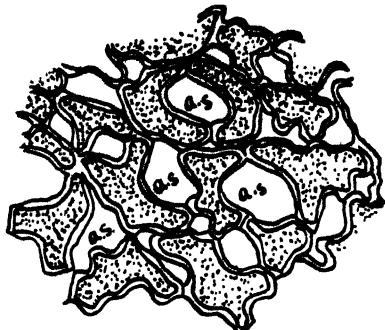
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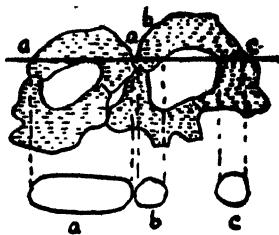
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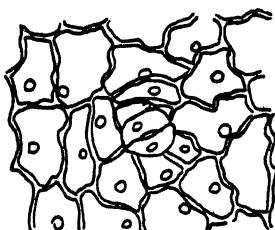
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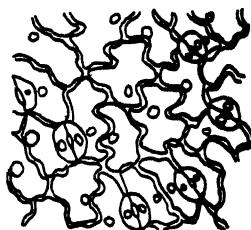
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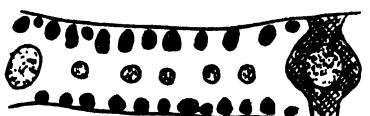
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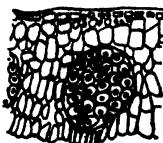
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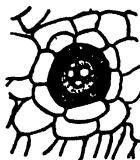
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Figs. 145–148.—*Smilax macrophylla* Roxb. : Fig. 145. Portion of the mesophyll as viewed from the surface : *a.s.*, air spaces. (× 240) ; Fig. 146. Diagrammatic representation showing how the lower mesophyll cells on being cut vertically appear some rounded and some transversely elongated. (× 240) ; Fig. 147. Upper epidermis (surface view) ; (× 240); Fig. 148. Lower epidermis (surface view). (× 240).

Figs. 149–154.—*Phoenix sylvestris* Roxb. : Fig. 149. T. S. of leaflet (diagrammatic) showing the distribution of vascular bundles (dotted) and sclerenchyma (cross-hatched). (× 80) ; Fig. 150. Upper epidermis (surface view). (× 240); Fig. 151. Lower epidermis (surface view) (× 240) ; Fig. 152. Portion of T. S. of leaflet showing the double-layered epidermis, and fibrous strand. (× 240); Fig. 153. Mesophyll containing vascular bundle and its sheath. (× 240) ; Fig. 154. Portion of T. S. of leaflet showing the double layered lower epidermis, and fibrous strand. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

Phoenix sylvestris Roxb.

The Wild Date-Palm of India is a very graceful tree, 30–50 feet high. Its trunk is rough with the persistent bases of the leaf-stalks and is surmounted by a hemispherical crown which is very large and thick (2). The tree is tolerably common throughout India, wild or more often cultivated. In the Bombay Presidency it is common in moist ground throughout the dry districts, usually along banks and in beds of streams and watercourses (10, 49).

The Leaf :

(*A*) *External Features.*—The leaves are 10–15 ft. long, greyish-green, quite glabrous, pinnate ; petioles compressed only towards the apex, at the base bearing a few channelled triangular short spines reaching 4 inches. Pinnules very numerous, densely fascicled, 6–18 by ¾–1 inch long, glaucous rigid, ensiform, folded longitudinally and attached obliquely with their folded bases to the woody common petioles (2, 10) (Fig. 9), subulately acuminated, almost spinous pointed, 2–4-farious, some intermediately spreading, others crossing these above and below in an ascending direction (2). Milne in his monograph on the Date Palm, *Phoenix dactylifera* Linn. (37), describes the morphological features of the leaf and its adaptations. As his remarks can fairly be made applicable to the leaves of *Phoenix sylvestris* also, we quote him : "Collectively these pinnae give far less resistence to winds than a single large undivided leaf blade would have done, and there is also less risk of the tree being overthrown, or its stem broken during a wind storm. Instead of the pinnae being arranged in one plane on either side of the main axis as in the case of the pinnae of a feather, they are usually arranged in two, and sometimes three or more, more or less distinct planes on either side of it. This arrangement also facilitates the passage of the wind between the leaflets". . . . "The leaflets of the date palm are folded once lengthwise, the two edges being turned upwards. At the base of the leaflet where it joins the main axis the fold is fixed, and is nearly complete, *i.e.* the two edges of the leaflet almost meet each other. When the palm has a plentiful water-supply and other conditions are favourable, each leaflet beyond its basal part is unfolded to expose as large a surface area as possible to the sun, thus allowing the chlorophyll to do its maximum work and to give the stomata on both the face and back of the leaflet the freest action, but when there is a scarcity of water the leaflet folds itself more or less tightly along its whole length, and the two halves of the face of the leaflet come together, thus protecting that surface of the leaflet from the dry winds and reducing the amount of moisture transpired from the plant. At the same time the leaflets tend to swing round and crowd more together, thus sheltering each other from the dry winds. These closing movements are caused by the contraction of a small pad of a yellowish tissue called a 'pulvinus' situated at the base of each leaflet." With regard to the spines at the base of the common petioles, he says that they "would assist in protecting the tender young terminal bud from damage by the larger animals.

(*B*) *Internal Structure.*—(Figs. 149–158). In essential respects the structure of the leaf of *Phoenix sylvestris* resembles that of the leaf of *P. dactylifera* described by Milne (57). The transverse section of the leaflet

is V-shaped in outline (Fig. 155). The epidermis (Figs. 150, 151, 152, 154) is two-layered, thick-walled and strongly cutinized. Its cells have an irregular outline in surface view. Apart from functioning as a water-proof covering the epidermis also forms a hard exoskeleton. The stomata (Figs. 150, 151, 158) occur on both surfaces. They lie on the epidermis opposite to the gaps between the fibrous strands. Their frequency is 272 and 336 per 1 sq. mm. on the upper and lower sides respectively. The guard-cells are sunken below the surface of the epidermis. They are thick-walled and provided with cuticular ridges. Above the cuticular ridges of the guard-cells project the cuticular ridges of the subsidiary cells, thus dividing the outer chamber into two com-partments. The mesophyll (Figs. 152, 153, 154) is composed of several layers of uniform palisade cells, which extend from epidermis to epidermis without any differentiation. The vascular bundles (Fig. 153) are situated in the mesophyll midway between the upper and the lower epidermis. The larger of these are embraced both on the upper and the lower side by fibrous sheaths, which, in some cases, extend from epidermis to epidermis, forming I-girders (Figs. 148, 155). The smaller vascular bundles may have internal and external fibrous sheaths, so as to constitute an internal girder. The position of this internal girder between the two surfaces of the leaf seems at first sight to have very little mechanical significance and in cases where fibrous sheaths are poorly developed, the mechanical advantage must obviously be local. Here the fibrous sheaths serve only to protect the individual vascular bundles. Vascular bundles unprovided with fibrous sheaths also occur along with those so provided. In addition to these internal girders there are a large number of sub-epidermal fibrous strands (Figs. 149, 152, 154, 155). They are, however, placed at irregular intervals and scarcely, if ever, it happens that two sub-epidermal strands lie opposite each other and combine to form a typical girder. Haberlandt (18) has observed precisely the same lack of correspondence between the sub-epidermal fibrous strands of opposite sides of the leaf in *Phoenix dactylifera* Linn. and in some other palms. The true significance of this peculiar arrangement of the mechanical tissue in many palm leaves has been explained by Haberlandt who, agreeing with Stahl (48), says that such leaves "are constructed so as to combine strength with pliancy ; the withdrawal of the mechanical strands from the periphery of the cross-section to the centre" "fully accords with the behaviour of the leaves in the wind." "The centralization of the mechanical tissue has the further advantage of increasing the resistance of the pinnae to the longitudinal tensions produced by the wind action."

In addition to the sub-epidermal girders there may also be found isolated strands in the mesophyll which have apparently no direct con-nection with the sub-epidermal strands or with vascular bundles. The sub-epidermal fibrous strands are specially enlarged at the margin, where also the epidermal cells as well as some layers of the mesophyll have become extremely thickened and sclerotic. The tip, where the leaflet narrows to a sharp hard point is entirely composed of this marginal strengthening tissue. This marginal strengthening tissue makes it almost impossible for the leaf to tear lengthwise under the pressure of strong wind. The mid-rib (Figs. 155, 156) contains no vascular bundles at all, and most of it is made up of mechanical tissue consisting of :

(*a*) thick-walled strongly cutinized epidermal cells, (*b*) the sub-epidermal and other fibrous strands and (*c*) thick-walled mesophyll cells, most of which are devoid of chlorophyll and are modified into mechanical tissue. It will thus be seen that the mid-rib for the most part performs the mechanical function. It has lost its usual function of translocation, as the need for it is dispensed with by the blades being directly attached by their folded margins to the woody common petiole. The structure of the leaflets is obviously xeromorphic and in keeping with the mechanical requirements necessitated by the habitat of the plant.

3. HERBS

Argemone mexicana Linn.

This is a prickly herb, 2–4 ft. high, long ago introduced from America, but now completely domiciled and widely distributed in India. It has been met with along roadsides, and as a weed in cultivated fields throughout the country. It occurs mostly in places where very few other plants thrive. The whole plant including the leaves has a complete covering of wax which gives it a glaucous appearance.

The Leaf :

(*A*) *External Features.*—The leaves are sessile and ½-amplexicaul variegated with white, 3–6 by 1–2½ ins., sinuate-pinnatified, with segments inciso-dentate, spiny on the margin, the midrib and the veins beneath (10).

(*B*) *Internal Structure.*—(Fig . 159–161). The leaf structure is dorsiventral. The epidermis is made up of very large tabular cells (Fig. 159) which appear irregular-shaped with somewhat straight walls in surface view (Figs. 160, 161). The cell-walls of the epidermal cells are slightly thickened and have a coating of wax. The stomata (Figs. 159, 160, 161) are almost equally distributed on both the surfaces, being 120 and 122 per 1 sq. mm. respectively on the upper and the lower epidermis. They are sunken below the general surface of the epidermis and are extremely small compared to the epidermal cells. The mesophyll is differentiated into a palisade of two or three layers and a loose spongy parenchyma. The vascular bundles of the smaller veins are embedded in the mesophyll of the leaf and are not strengthened by sclerenchyma. The mesophytic structure is easily understood if it be considered that the plant makes its appearance soon after the rains and passes its brief life under conditions of a fast drying—but by no means completely dry—soil and a progressively increasing insolation with the advance of the dry season for which, it would appear, that the coating of wax is sufficient protection.

PLATE XV
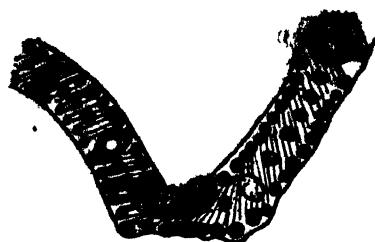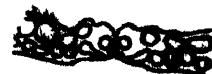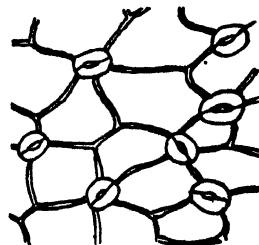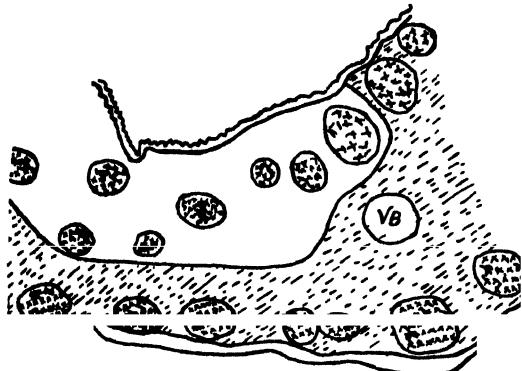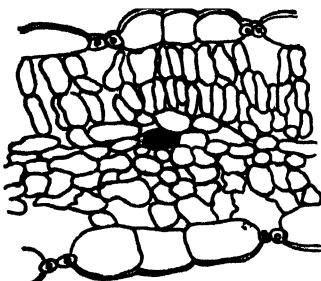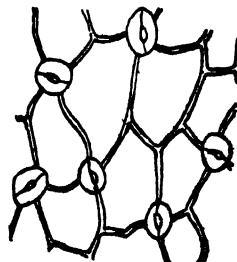
Figs. 155–158.—*Phoenix sylvestris* Roxb. : Fig. 155. Semidiagrammatic T. S. of the leaflet passing through the midrib showing distribution of tissues : Vascular bundles dotted ; mesophyll hatched, thickened tissues and sclerenchymatous strands cross-hatched. (× 80) ; Fig. 156. Portion of midrib of leaflet (semi-diagrammatic) (highly magnified) ; Fig. 157. Portion of the leaf showing the mode of attachment of the leaflets to the woody common petiole ; Fig. 158. Stoma in V. S. (× 540).

Figs. 159–161.—*Argemone mexicana* Linn.: Fig. 159. T. S. of leaf. (× 240); Fig. 160. Lower epidermis (surface view). (× 240); Fig. 161. Upper epidermis (surface view). (× 240).

N.B.—The figures have been reduced in reproduction To get the initial magnification indicated after each figure multiply by 2.1.

Caesulia axillaris-Roxb.

This is a succulent prostrate or suberect herb 16–18 ins. high. It is very common in rice fields and other marshy places where it passes the earlier period of its life history living as an aquatic or marsh plant. The plant can live just as well as an ordinary land plant in the dry season. During the rains the rice fields and other places where it thrives are covered with water and the plant is an aquatic or marsh plant. After the rains as the soil becomes dry the plant lives under ordinary land conditions. There should obviously be some differences between the aquatic and dry stages of the plant.

The Leaf:

(A) *External Features.*—The leaves are sessile 1½–6 by $\frac{3}{16}$—1 in., lanceolate, acute, distantly serrulate, narrow at the base, glabrous (10). Under marsh conditions the leaves have their edges directed horizontally, but when the ground dries up and conditions become xerophytic, they assume a profile lie.

(B) *Internal Structure.*—(Figs. 162–167). The epidermis consists of tabular cells which in surface view show irregularly wavy outlines. Stomata are found on both surfaces. The guard-cells lie on a level with the ordinary epidermal cells and are provided with prominent cuticular ridges (Fig. 164). The mesophyll in the case of the leaf examined in October (Fig. 167) is seen to be composed of uniform cells, but a green photosynthetic tissue (hatched in Fig.) made up of cells packed with chloroplasts is distinguishable from a clearer area in the centre (dotted in Fig.) the cells of which contain relatively fewer chloroplasts. The clearer area is seen in transverse section to occupy the regions of the midrib and to extend into the blade on either side in the form of a wing dividing the photosynthetic tissue into an upper and a lower part. In this clearer area are situated the vascular bundles (cross hatched in Fig.) and well-defined lacunae (unshaded in Fig.) In the leaf examined in February when drier conditions prevail (Fig. 163), the following differences are observed :—The cell walls of the epidermal cells are more thickened and cutinized. There are no well-defined lacunae seen in the clearer area of the mesophyll. The photosynthetic tissue shows cells which tend to be elongated in palisade fashion. The isobilateral structure of the leaf seems to be due to the fact that the leaves are not placed quite horizontally but point skywards. On the whole, the structure, though in essential respects mesophytic, is more or less plastic in regard to the water relation, *i.e.* shows a tendency towards xerophytism under drier conditions.

PLATE XVI

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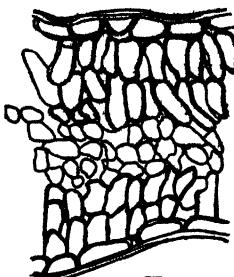
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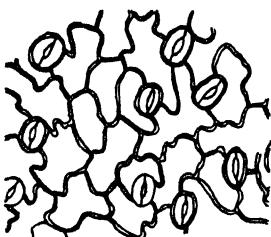
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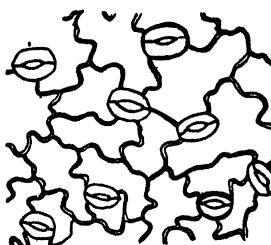
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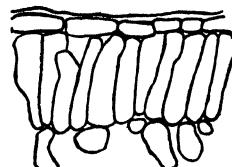
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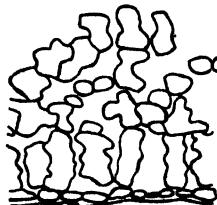
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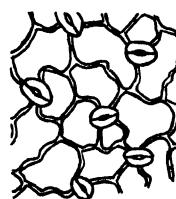
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Figs. 162–167.—*Caesulia axillaris* Roxb. : Fig. 162. T. S of leaf (diagrammatic):
Photosynthetic tissue hatched ; clear central mesophyll shaded with dots. (× 16);
Fig. 163. T. S. of leaf. (× 240); Fig. 164. Stoma in V. S. (× 540); Fig. 165.
Upper epidermis (surface view). (× 240) ; Fig. 166. Lower epidermis (surface view).
(× 240); Fig. 167. T. S. (diagrammatic) of the leaf : The photosynthetic tissue is
hatched ; the vascular bundles are cross-hatched, and the remaining mesophyll tissue
is shaded with dots. (× 12).

Figs. 168–171.—*Eclipta erecta* Linn. : Fig. 168. Portion of upper epidermis with
palisade tissue in T. S. (× 240) ; Fig. 169. Portion of lower epidermis with spongy
tissues in T. S. (× 240) ; Fig. 170. Lower epidermis (surface view). (× 240) ; Fig.
171. Upper epidermis (surface view). (× 240).

N.B.—The figures have been reduced in reproducion. To get the initial magnifi-
cation indicated after each figure multiply by 2.1.

Eclipta erecta Linn.

It is an erect or prostrate, branched herb, often rooting at the nodes with stem and branches strigose with appressed white hairs. It is one of those plants which can grow in damp places or in dry situations with comparative ease. It is very common in ricefiel dsand in other marshy places. It seems to be quite indifferent as to its habitat, but prefers damp situations and is often found growing in water with its lower portions submerged. It is also capable of thriving in the dry season in very dry soil.

The Leaf :

(*A*) *External Features.*—The leaves are sessile, 1-3 ins. long, variable in breadth, usually oblong-lanceolate, sub-entire, acute or subacute, sparsely strigose with appressed hairs on both sides, base tapering (10).

(*B*) *Internal Structure.*—(Figs. 168-174). The epidermis is made up of tabular cells (Figs. 168, 169) which in surface view appear wavy in outline (Figs. 170, 171). The thickening of the walls and the extent of the cutinization depend upon the conditions under which the plant is growing whether as marsh plant or in drier conditions. The stomata (Figs. 170, 171, 172, 174) are not sunken and show no special devices for checking transpiration, except the cuticular ridges and the variable thickening of the walls of the guard-cells. Protective hairs occur on both upper and the lower surfaces. They are multicellular and are rather thick-walled, many appearing encrusted (Fig. 173). The mesophyll is of the mesophytic type consisting of a palisade of one to two layers of cells and a spongy parenchyma of loosely arranged irregular-shaped, often multiradiate cells.

Stemodia viscosa Roxb.

This is an erect, much-branched, aromatic herb, 3-24 ins. high with stem and branches angular and viscidly pubescent (10). It occurs in wet places specially in the ricefields. The earlier stages of the plant are passed in water or in water-saturated soil. But at the time of flowering, since the fields gradually dry up, the plants appear like ordinary meso- phytes.

The Leaf :

(*A*) *External Features.*—The leaves are variable, $\frac{1}{2}$ -1$\frac{3}{4}$ by $\frac{1}{4}$-$\frac{1}{2}$ ins., sessile, usually oblong acute (rarely obovate), serrulate or subentire, glandular pubescent or nearly glabrous, usually tapering, often cordate and amplexicaul at the base (10).

PLATE XVII.
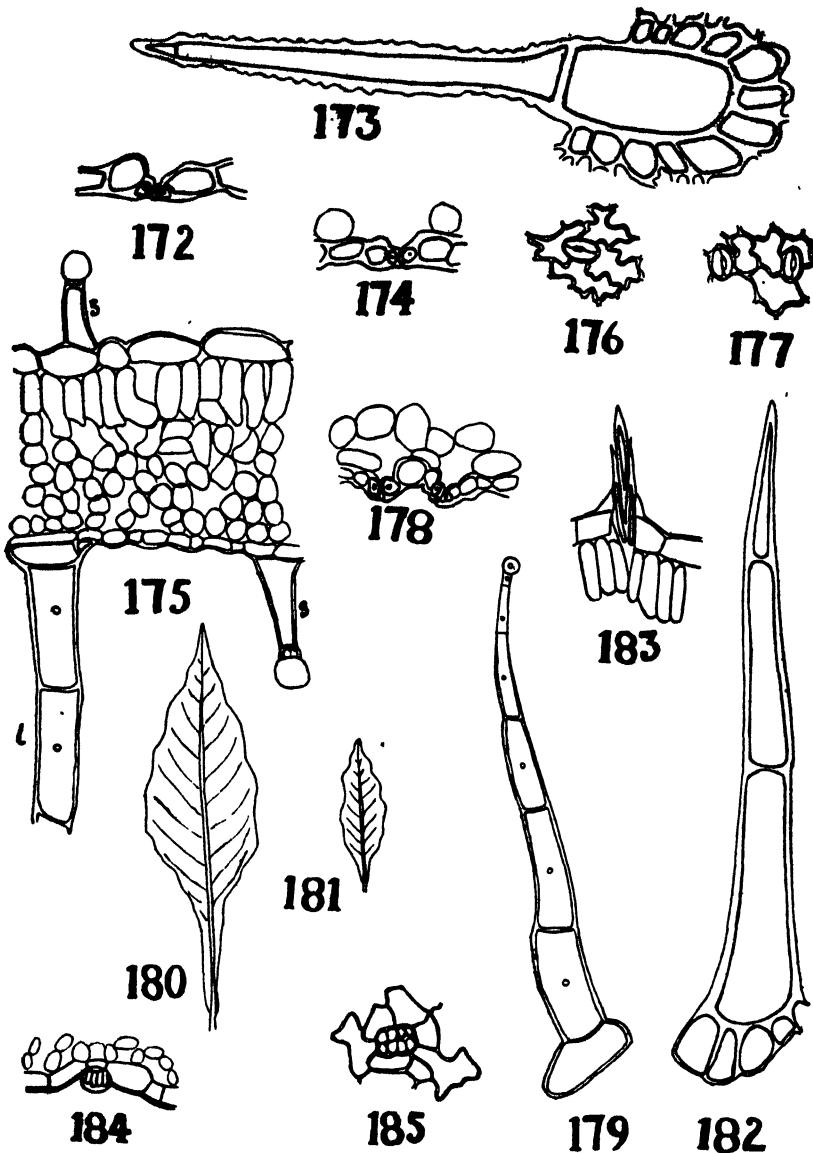
Figs. 172–174.—*Eclipta erecta* Linn. : Fig. 172. Stoma from upper epidermis in
V. S. (× 540) ; Fig. 173. A hair. (× 210) ; Fig. 174. Stoma from lower epidermis in
V. S. (× 540).

Figs. 175–179.—*Stemodia viscosa* Roxb. : Fig. 175. T. S. of leaf. (× 240); Fig.
176. Lower epidermis (surface view). (× 240); Fig 177. Upper epidermis (surface
view). (× 240) ; Fig. 178. Stomata in V. S. (× 540) ; Fig. 179. A glandular hair.
(× 540).

Figs. 180–185.—*Hygrophila spinosa* T. Anders. : Fig. 180. Leaf of shade plant.
(nat. size) ; Fig. 181. Leaf of sun plant. (nat. size) ; Fig. 182. Uniseriate hair from
sun-leaf. (×240); Fig. 183. Multiseriate hair from shade leaf. (× 240) ; Fig. 184.
Glandular hair in V. S. (× 240) ; Fig. 185. Glandular hair in surface view. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnifi-
cation indicated after each figure multiply by 2.1.

(*B*) *Internal Structure.*—(175-179). The leaf-structure is bifacial. The epidermis (Figs. 175, 176, 177) of both the surfaces consists of somewhat moderately thick-walled tabular cells with wavy outlines in surface view. Stomata occur on both the surfaces and are prominently exposed (Fig. 178). They are of the ordinary type with prominent cuticular ridges whose close approximation is responsible for their closure (18). Glandular hairs are of two types : (*a*) short ones having a large head and a stalk consisting of two cells (Figs. 175,*s*) and (*b*) longer tapering ones with a tapering stalk of several cells topped by a correspondingly smaller head (Fig. 175, *l* & Fig. 179). The mesophyll consists of a single layer of palisade cells and an ordinary spongy parenchyma composed of loosely arranged rounded or irregular-shaped cells. The structure is mesophytic.

Hygrophila spinosa T. Anders. (=*Asteracanthu longifolia* Nees)

This is a stout herb with numerous fasciculate usually unbranched subquadrangular erect stems, 2-5 ft. high, thickened at the nodes, more or less hispid with long hairs, especially below each node (10). The plant is very common on marshy ground and grows luxuriantly in the shade of trees. In extremely dry conditions which prevail before the rains, the plant dies down to the surface of the ground perennating only by the underground portions.

The Leaf :

(*A*) *External Features.*—The leaves are sparsely hispid on both sides, tapering at the base, sessile (or at least without clearly defined petioles), in verticils of 6 at a node, the two outer leaves of the whorl large, reaching 7 by $\frac{1}{2}$-$1\frac{1}{2}$ ins., oblong lanceolate or oblanceolate, the 4 inner leaves reaching about $1\frac{1}{4}$ ins. long, each of the 6 leaves with a nearly straight sharp yellow spine, 1-$1\frac{3}{4}$ ins. long, in its axil (10). The leaves studied by the present writer were of plants growing in sun and shade. The plants were growing in damp fields or in fields in which the soil had become dried up and sun-cracked. Some leaves were also obtained from plants growing in the shade of trees in damp places on the banks of the Povai Lake in Salsette Island. Figs. 180 and 181 give a relative idea of the dimensions of the leaves under sun and shade conditions. In plants growing fully exposed to the sun, leaves have very narrow laminae compared to those of plants which live in the shade of trees.

PLATE XVIII
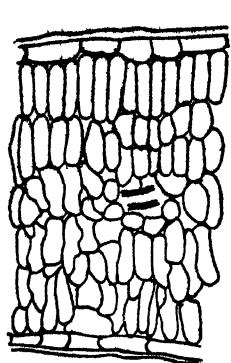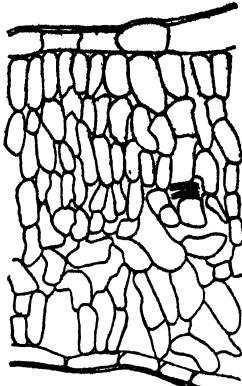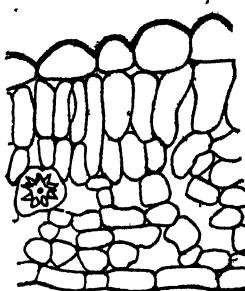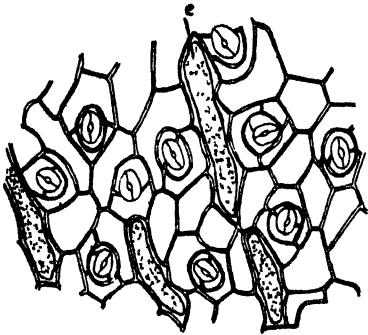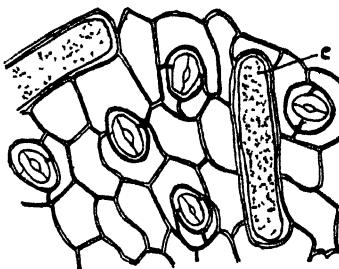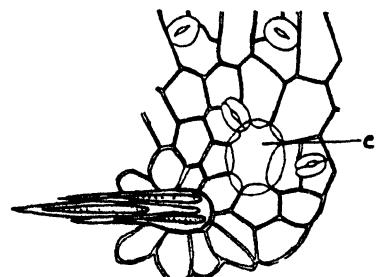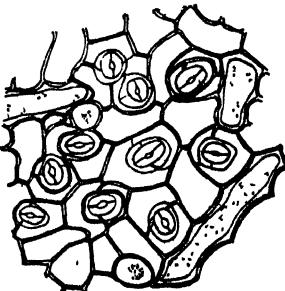
Figs. 186-192.—*Hygrophila spinosa* T. Anders.: Fig. 186. T. S. of leaf from sunny dry field. (× 240); Fig. 187. T. S. of leaf from sunny damp field. (× 240); Fig. 188. T. S. of shade-leaf (× 240); Fig. 189. Upper epidermis (surface view) from sunny dry field. (× 240); Fig. 190. Upper epidermis (surface view) from sunny damp field. (× 240); Fig. 191. Upper epidermis (surface view) from shady damp field. (× 240); Fig. 192. Lower epidermis (surface view) from sunny dry field. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

*(B) Internal Structure.*—(Figs. 180–195). The epidermis is made up of more or less regular-shaped cells with the outer cell-walls thickened and cutinized in plants of sunny places. The cuticle is thicker in leaves of plants growing in the sun in drier situations (Fig. 186) than in damp fields (Fig. 187). In shade plants the outer walls of the upper epidermal cells are convex (Fig. 188) and protrude as in many other shade plants in a papillose manner and act, as has been suggested by Haberlandt (18), as "condensing lenses converging the available light upon the chlorophyll which lies on the lateral walls of palisade cells." This structure is in keeping with the shade requirement of the plant. Both the upper and lower epidermal cells (Figs. 189–195) of the sun-leaves are larger than those of the shade leaves. The stomata in the sun-leaves have each a pair of narrow horse-shoe shaped subsidiary cells surrounding them to form a ring. No such subsidiary cells are noticed in the case of the shade leaves. The significance of these subsidiary cells in the case of the sun plant could not be ascertained. In both sun and shade leaves the guard-cells are on a level with the surface. The number of stomata per unit area (1 sq. mm.) in leaves growing in the three situations studied, were as follows :—

| | | Sun leaves | | Shade leaves |
		Dry field	Damp field	Damp situation
Upper	..	130	150	116
Lower	..	160	176	140

As the results were conflicting no interpretation of their respective frequency was attempted. In the plants growing in the sun-lit fields, whether dry or damp, uniseriate hairs with thick walls occur on both surfaces of the leaf specially along the veins (Fig. 182). These uniseriate hairs are not found on leaves growing in shade ; in their place there are found both on upper and lower surfaces multiseriate trichomes (shaggy hairs) (Figs. 183, 191, 194). It appears that uniseriate hairs which are abundant in young sun-leaves but become fewer in older leaves seem to serve as a screen against the excessive illumination which the leaf is exposed to before the cuticle is formed. Their absence in the shade leaves, at all stages, would suggest that the protection against excessive illumination is not called for. In the shade leaves instead of the uniseriate hairs we have multiseriate trichomes (shaggy hairs) whose shape suggests that their action is purely mechanical, it would seem, against possible marauders such as snails and other animals by which these plants are liable to be infested. The writers are inclined to the view that these multiseriate (shaggy) hairs are modifications of uniseriate hairs with reference to their change of function. The cutting down of the illumination in the case of the said plant having dispensed with the need for protection against such illumination, the energy of the leaf is diverted to the formation of stronger structures (multiseriate hairs) which would be effective against the attacks of animals. It would also appear that shade conditions foster luxuriant development of all structures including the hairs which in the case of this plant, from being merely uniseriate, become multiseriate. Glandular hairs (Figs. 184, 185) so common in the order *Acanthaceae* (43) occur in all leaves. Oblique cystoliths (Figs. 189, 190, *c*) are seen in the epidermis of the sun leaves. They are scarcely represented

in the shade leaves, where only the cells enclosing them may be seen
(Fig. 191, c). The mesophyll of the leaves growing in lighted situations
(Figs. 186, 187) is more massive than in the shade leaves. There is
scarcely any differentiation into palisade and spongy tissue, all cells
being more or less elongated in a plane at right angles to the epidermis,
only that in the leaves of plants growing in damper situations, the lower
part of the mesophyll is of a looser texture owing to the presence of large
air-spaces (Fig. 187). The shade leaf (Fig. 188) is relatively thinner
than the sun-leaf, and its mesophyll is clearly differentiated into a palisade
tissue of two layers and a loose spongy parenchyma. It will be seen
from the above account that the leaves are mesophytic but extremely
plastic.

Alternanthera sessilis R. Br. (=A. triandra Lam.)

This is a herbaceous plant much branched from the root ; branches
6-20 ins. long, often purplish, prostrate or ascending, often rooting at
the lower nodes (10). The plant is amphibious and is capable of growing
practially submerged in water as well as on land. It generally occurs
in damp places throughout the warmer parts of India, Ceylon and other
countries.

The Leaf :

(A) *External Features.*—The leaves are ½-2 by ⅛-⅔ ins. (in wet
places sometimes reaching 4 by 1 in.) somewhat fleshy linear oblong,
lanceolate or elliptic, obtuse or subacute, sometimes obscurely denti-
culate, shortly petiolate, glabrous (10).

(B) *Internal Structure.*—(Figs. 196-200). The upper and the lower
epidermis consist of tabular cells (Fig. 196) which have more or less
wavy outlines in surface view (Figs. 199, 200). The number of stomata
on the upper and the lower surfaces is 160 and 306 respectively per
1 sq. mm., *i.e.* they number twice as many on the upper surface. The
guard-cells (Figs. 197, 198) are not sunken but show strong outer cuti-
cular ridges. The thickness of the walls and the cutinization of the
epidermal and guard-cells varies according to the habitat, being stronger
the drier the habitat. The palisade tissue consists of three to four layers
of longer or shorter cells. The spongy parenchyma is of irregular-
shaped isodiametric cells, with the size of the air-spaces varying with the
humidity of the soil. Conglomerate crystals occur in the mesophyll.
It will thus be seen that the leaf structure is plastic being mesophytic
when the plant grows in damp situations and having a tendency towards
xerophytism in drier situations.

PLATE XIX
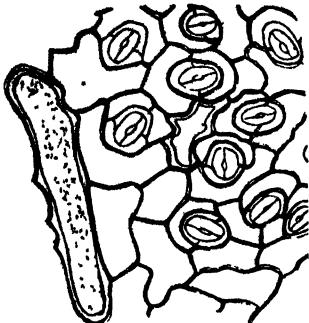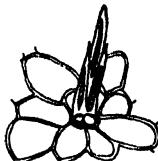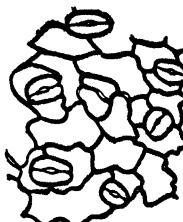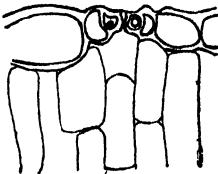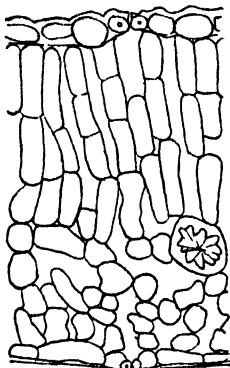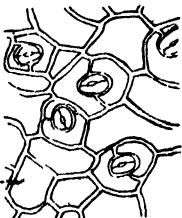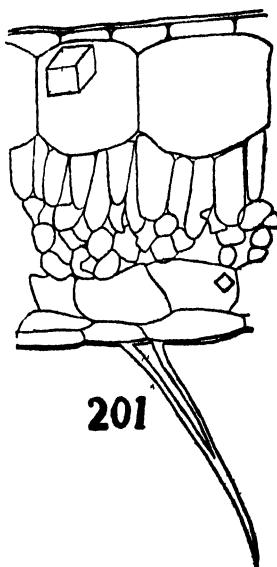
Figs. 193 -195.—*Hygrophila spinosa* T. Anders. : Fig. 193. Lower epidermis (surface view) from sunny damp field. (× 240); Fig. 194. Lower epidermis (surface view) from shady damp field showing mult iseriate hair. (× 240); Fig. 195. Lower epidermis (surface view) from shady damp held. (× 240).

Figs. 196–200. —*Alternanthera sessilis* R. Br.: Fig. 196. T S. of leaf. (× 240); Fig. 197. Portion of T. S. of upper epidermis showing stoma in V. S. (× 540); Fig. 198 Portion of T. S. of lower epidermis showing stoma in V. S. ; Fig. 199. Upper epidermis (surface view). (× 240); Fig. 200. Lower epidermis (surface view). (× 240).

Figs. 201.—*Costus speciosus* Smith : T. S. of leaf. (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

II (4)

Costus speciosus Smith

This is an erect herbaceous plant with long leafy stems 4–9 ft. high ; rootstock tuberous ; stem sub-woody at the base. It is a very common plant usually forming an undergrowth in the better lighted parts of the deciduous forests where the plant luxuriates in the rains under very warm humid conditions. In the dry season the plant dies down to the surface of the ground and perennates by means of its underground rhizome which also helps to propagate and spread the plant. It occurs in Salsette and many other places of the Presidency including Khandala and Castle Rock.

The Leaf :

(A) *External Features.*—The leaves are provided with broad coriaceous sheaths. They are 6–12 by 2¼–3 ins., subsessile, spirally arranged, oblong or oblanceolate-oblong, acute or acuminate, often cuspidate, glabrous above, silky-pubescent beneath, base rounded (10).

(B) *Internal Structure.*—(Figs. 201–205). A transverse section of the leaf (Fig. 201) shows a two-layered epidermis on both the upper and lower surfaces enclosing a centrally placed mesophyll. The inner (hypodermal) layers of both sides consist of thin-walled, squarish cells which are much larger than the cells composing the epidermis proper. The latter are tabular in form and have straight walls in surface view (Figs. 202, 204, 205). Cubical crystals and crystal groups occur in the hypodermal cells. De Bary (13) p. 411 has referred to the occurrence of hypodermal layers in the leaves of several plants including some Scitaminaceae, such as *Musa, Sterlitzia, Heliconia, Canna* and even *Costus* sp. The double epidermis in *Costus speciosus*, consisting of the epidermis proper and hypoderma, is entirely devoid of chloroplasts and represents a peripheral water tissue of the type occuring in *Begonia* (12), *Canna, Maranta* and *Tradescantia* in which plants according to Haberlandt, "the need for water storing arrangement is felt on account of the large delicate leaves in which transpiration attains enormous proportions under the influence of the prevailing intense insolation" (18) whose effect, as Schimper (46) has remarked in the case of plants living in similar situations, is strikingly enhanced under the moist monsoon conditions in which *Costus* lives. The outer walls of the epidermal cells of both the surfaces are moderately thickened. The upper epidermis is altogether devoid of hairs, but on the lower side the hairs are abundant, being, in the specimens examined, on an average 28 per 1 sq. mm. The hairs (Figs. 201, 202) are uniseriate. They are placed on rounded cells of the epidermis and are in the form of long tapering structures, each made up of a short basal cell (b) and a long distal tapering cell (c). The outer walls of the hairs are very thick. The hairs seem to be protective adjustments against transpiration. Stomata (Figs. 202, 203, 204) are present on both the surfaces. They are on an average 4 and 24 per 1 sq. mm. on the upper and lower sides respectively. The guard-cells are on a level with the general surface of the epidermis. Only the outer cuticular ridges are well developed. It appears that their approximation on closure of the stomata affords, as Haberlandt (18) p. 466 has suggested in the case of floating aquatics and other plants inhabiting moist situations, sufficient protection against excessive transpiration under the

PLATE XX

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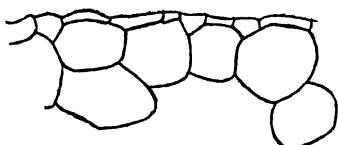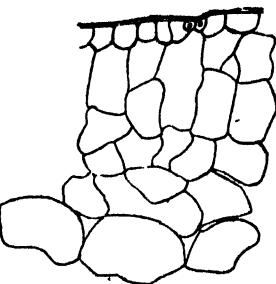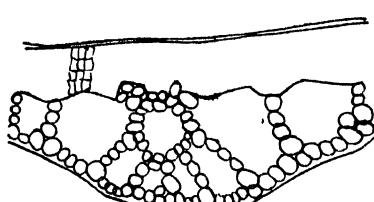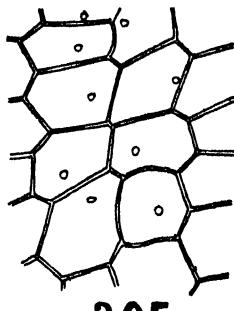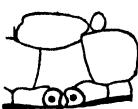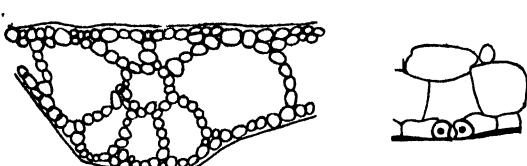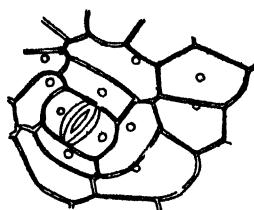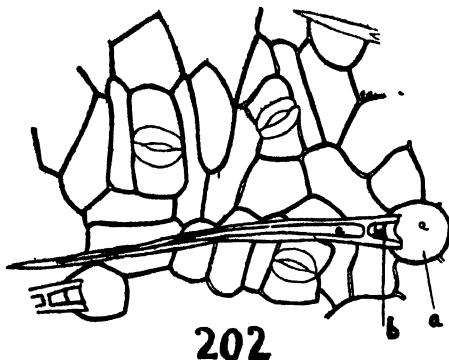
Figs. 202–204.—*Costus speciosus* Smith : Fig. 202. Lower epidermis in surface view. (× 240) ; Fig 203. Stoma in V. S. from lower epidermis. (× 240) ; Fig. 204. Stoma in surface view from upper epidermis, (× 240), Fig. 205. Upper epidermis (surface view). (× 240).

Figs. 206–209.—*Aponogeton monostachyon* Linn. : Fig. 206. T. S. at midrib of submerged leaf. (× 80); Fig. 207. T. S. at midrib of floating leaf. (× 80) ; Fig. 208. Portion of the upper epidermis of the midrib of submerged leaf. (× 240) ; Fig. 209. Portion of the upper epidermis of the midrib of floating leaf (× 240).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1.

humid monsoon conditions in which the plant lives. The mesophyll is centralized. It consists of a single layer of funnel-shaped palisade cells below which is a spongy parenchyma consisting of loosely arranged isodiametric cells recalling the structure seen in Begonia (12). The structure on the whole is mesophytic.

Aponogeton monostachyon Linn.

This is an aquatic herb growing in tanks in several places in the Bombay Presidency and throughout India. It has a root-stock ½–¾ in. in diameter (10).

The Leaf :

(A) *External Features.*—Cooke (10) describes the leaves as floating; the plant however displays heterophylly as in certain *Potamogetons* (1). Floating as well as submerged leaves occur. They may appear simultaneously on the plant or one type or the other may be absent. The floating leaves have petioles which vary in length with the depth of the water so as to permit the lamina to lie flat on the surface of the water. The laminae of the floating leaves are 2½–8 by ¾–1½ ins., oblong or linear-oblong acute or obtuse, base cuneate, rounded or cordate, 3–5-nerved and with numerous distinct cross nervules between them (10). They are more or less opaque with a dark-green colour and shining upper non-wettable surfaces as in *Potamogeton, Nymphaea* and *Limanthemum* (1) which in the case of *Potamogeton,* according to Lundstrom (32) are due to an oily substance secreted by special colourless plastids of the epidermal cells. The submerged leaves have shorter petioles, and more or less lanceolate pale green, translucent laminae having undulated margins as in certain species of *Potamogeton* (1), and also in *Aponogeton ulvaceus* Baker (29).

(B) *Internal Structure.*—(Figs. 206–218). The lamina of the floating leaf of *Aponogeton monostachyon* corresponds in structure to the floating laminae of other aquatics such as *Nymphaea, Limanthemum* and more particularly *Potamogeton* (1). It has a dorsiventral structure (Figs. 207, 213). The upper epidermis consists of a single layer of more or less tabular cells (Figs. 209, 213) which in surface view show an irregular outline (Fig. 215). The outer walls of the upper epidermal cells show slight thickening. The stomata (Figs. 215, 218) are confined only to the upper epidermis. They communicate with the air-spaces of the spongy parenchyma by means of passages which run through the rows of palisade cells. The stomata are of the aquatic type whose closing is effected according to Haberlandt p. 466 (18) by the approximation of the well developed outer cuticular ridges. They number 184 per 1 sq. mm. The lower epidermis is also composed of somewhat tabular cells (Figs. 211, 213) with wavy margins in surface view (Fig. 217), but the cell-walls are thin. The palisade (Fig. 213) consists of rows of cells elongated at right angles to the upper surface and is of a looser texture than in ordinary land plants. The cells of the palisade are heavily charged with chloroplasts. The spongy tissue (Fig. 213) consists of irregular-shaped cells with large intercellular spaces between them. Except the lowermost layer, the cells of this tissue tend to be elongated

PLATE XXI
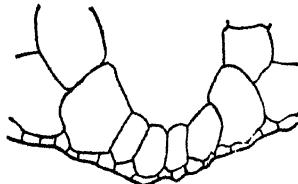
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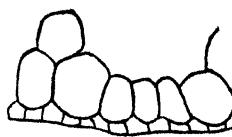
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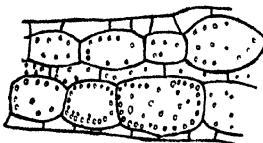
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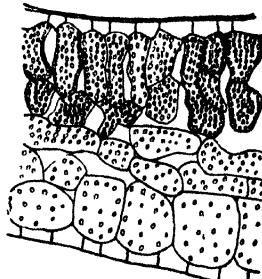
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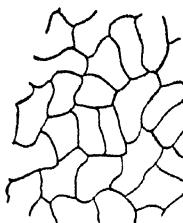
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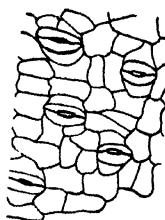
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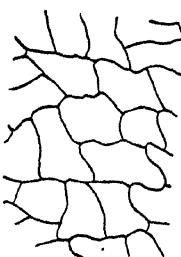
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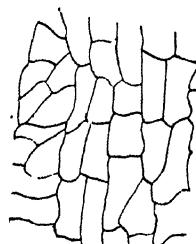
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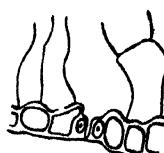
218

Figs. 210–218.—*Aponogeton monostachyon* Linn.: Fig. 210 Portion of the lower epidermis of the midrib of submerged leaf. (× 240); Fig. 211. Portion of the lower epidermis of the midrib of floating leaf. (× 240); Fig. 212. T. S. of the blade of submerged leaf. (× 240); Fig. 213. T. S. of the blade of floating leaf. (× 240); Fig. 214. Upper epidermis (surface view) of submerged leaf. (× 240); Fig. 215. Upper epidermis (surface view) of floating leaf. (× 240); Fig. 216. Lower epidermis (surface view) of submerged leaf. (× 240); Fig. 217. Lower epidermis (surface view) of floating leaf. (× 240); Fig. 218. Stoma from floating leaf in V. S. (× 540).

N.B.—The figures have been reduced in reproduction. To get the initial magnification indicated after each figure multiply by 2.1

in a direction parallel to the surface of the leaf though most of them appear isodiametric. The spongy cells contain fewer chloroplasts than the palisade cells. The lowermost layer of the mesophyll consists of cells of larger dimensions compactly arranged. In the region of the midrib (Fig. 207) the air-spaces in the spongy parenchyma assume the size of lacunae. The structure of the submerged leaf (Figs. 206, 208, 210, 212, 214, 216) differs from that of the floating leaf (Figs. 207, 209, 211, 213, 215, 217, 218) in the following details which show agreement with other submerged leaf types : (1) The epidermis of both sides is made up of extremely thin-walled cells which contain chloroplasts. (2) Stomata are absent from both surfaces. (3) The blade portion is much thinner than in the floating leaf and its mesophyll is made up of only three layers of compactly arranged cells in which there is no differentiation into palisade and spongy. (4) In the midrib the lacunae are much larger and there is also no differentiation into palisade and spongy. The structures of both the floating and submerged leaves are well adapted for their respective requirements. The floating leaf with its stomata on the upper surface is adapted for the assimilation of carbon-dioxide from the air, and the submerged leaf with its thin cell-wall and without stomata for assimilation of dissolved carbon-dioxide.

CONCLUSION

A study of the various leaves described in this treatise reveals in the case of tropical forest trees and shrubs—whether evergreen or deciduous —a xerophytic structure which appears to be scarcely affected by the change of seasons with its alternation of wet and dry periods. In other words, to use Thoday's terminology, these leaves are "xeromorphic" (50).

Another striking feature is the fact that in the case of the trees and shrubs studied, there is no differentiation in structure evident between the leaves of tropical evergreen plants on the one hand and deciduous plants on the other, as has been observed by Warming (52) between the leaves of evergreen and deciduous plants of cold temperate countries. In these climates the evergreen trees, since they are exposed to hard conditions in winter, i.e. to cold (physiologically dry) soil and possibly concurrent rapid transpiration caused by dry cold winds, have xerophytic leaves, while in the deciduous plants of the same regions the leaves which are ultimately shed are thinner, paler green, more flexible and with a cuticle thinner, and so on ; in other words they are typically mesophytic. In the case of the tropical trees and shrubs studied, with one notable exception (*Euphorbia nerufolia* Linn.), all the leaves whether evergreen or deciduous are typically xerophytic and they show no indication of more or less xerophytism as do the evergreen and deciduous leaves respectively of temperate countries. The reason for a xerophytic structure in tropical deciduous leaves seems to be that they become exposed to a longer or shorter period of drought conditions, for in most cases it happens that though the leaf-shedding takes place sometime during the dry period, the leafless condition of the plants does not synchronize with the driest period of the year. On the contrary it is often of a brief duration, and the new flush of leaves comes out and remains

on the trees long before the rains, when conditions are at their severest (15). Frequently the leaf fall is a sign that the tree is preparing to blossom, and it has been suggested that the fall of leaves in such cases is due to the fact that the swelling buds draw the transpiration current to themselves (46). In any case the fall of leaves and the appearance of new leaves are dependent to a great extent on internal factors (25, 46) rather than on the direct influence of the environment. The extreme xerophytic structure of the leaves of such deciduous trees which become exposed to longer or shorter periods of extreme drought conditions is thus explained. The exception above referred to concerns *Euphorbia nerifolia* Linn. which has mesophytic leaves adapted for the moist monsoon conditions obtaining when the plant is in leaf.

In the case of the herbs studied it is found that the leaves are plastic, *i.e.*, they show a facility to modify their structure in reaction to external factors, chiefly the presence or absence of water in the soil or about the plant. When such leaves show xerophytic structures, they are of the type called "xeroplastic" by Thoday (50). This plasticity is more evident in the leaves of amphibious plants.

It is not necessary, here, to enumerate the various features of leaf structure as these have been dealt with sufficiently in the body of the work. Only one point, to the writers' minds, not sufficiently stressed before need be mentioned here. A very striking feature of the leaves of many forest trees is the strong and often close reticulate venation that, in addition to serving as a mechanical framework to safeguard against tearing and as a network of conduits keeping all the parts of the leaf in communication and equalising the water supply at different points in the photosynthetic systems (18), marks off definite areas of leaf tissue which become so many photosynthetic centres or units. Often the veins which form meshes embedded in bridges of tissue extend from epidermis to epidermis and may further be strengthened with sclerenchyma. When this happens the photosynthetic units bounded by the meshes become isolated water-tight compartments so that in the case of accidental injury to any unit there is no danger from dessication to the neighbouring units or to the rest of the leaf. The bridges of tissue enclosing the veins also serve as girders keeping apart the two surfaces of the leaf. It has been observed that in leaves in which this girder-system is well-developed the mesophyll, especially the spongy tissue, is of a looser texture, the need for a more compact mesophyll being dispensed with.

The various types of leaf structure observed can thus be looked upon as so many contrivances to meet the requirements of the plant in regard to the vital processes-that are taking place in the leaf and to supply the mechanical strength that is necessary to be put up by the leaf under the various conditions to which it is subjected. In other words, the method of construction of leaves is, as Bower (7) considers in the case of all plant organs, a compromise between "the need for mechanical strength and for carrying out the vital processes."

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THE SIZE (DIAMETER) OF THE HUMAN RED BLOOD CELL

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WITH the differentiation of anæmias into the two types macro-cytic and microcytic the determination of the size (diameter) of the human red blood cell has become a subject of primary import-ance in clinical haematology for diagnostic and therapeutic purposes. It is hence necessary to have an accurate idea about the size of the normal red blood cell.

A reference to the different textbooks on physiology gave the following information : Howell's (1937) textbook gives 7.7 μ as the size. Halli-burton's (1935) Handbook of Physiology says "it is 8.8 μ on the average." Starling's (1936) Principles of Human Physiology says "it is 8.8 μ in the body. In the dried fixed film the average size is 7.2 μ (range 6.7 to 7.7 μ)." Wiggers's (1939) Physiology in Health and Disease says "it is 7 to 8 μ on slides. In the circulation it is probably larger, 8.8 μ, and subject to variations owing to diffusion and osmosis factors." Schafer's (1929) Essentials of Histology gives "the average diameter of human red corpuscle is stated to be 7.5 μ but Ponder, Millar and Dryerre by measuring the corpuscle in plasma say it is 8.8 μ with variations in health between 6 and 9 μ." An older book by Buchanan (1909) on haematology gives "Hayem classifies them (red cells) as large 8.5 μ, medium 7.5 μ, and small 6.5 μ. About 75% are medium and the rest equally divided between the other two classes."

One can see from the above how varied are the opinions and how vague our knowledge about the size of the normal human red cell. The discrepancy may be due to the different methods used by the different workers in the line.

METHODS

Almost all the figures for the size of the red cell given in books on Physiology or Medicine refer to it as determined in a blood film prepared in the usual way, that is, on a dried and fixed film either stained or unstained.

With the aid of a micrometer scale cells can be measured directly under a microscope with a known magnification and the average size of a single cell worked out from this. The process is however tedious and entails a lot of eye strain and error. It is therefore not in use now.

Price-Jones (1910), who first emphasised the importance of the macrocyte as a diagnostic feature in pernicious anaemia, uses a method in which by a special prism attached to the eyepiece of the microscope the image of the film is thrown down on to a paper. The eyepiece and the objective are chosen to give a magnification of one thousand. The outlines of the cells projected as images are then drawn accurately on the paper. 500 cells at least are thus drawn and their diameters measured with a glass mm. scale. By using statistical methods the mean diameter, the standard deviation and the coefficient of variation are calculated and compared with the normal by drawing a curve. This method is laborious, highly technical and requires a knowledge of statistical methods. It is not applicable for routine work but is used in difficult and selected cases. It is however claimed that this method not only gives an accurate idea of the cell size but also of anisocytosis which is at times the only corpuscular change associated with some rare cases of pernicious anaemia not accompanied by the usual macrocytosis.

Price-Jones's method has since been simplified by using a camera lucida for drawing the outlines. The method is quicker but less accurate.

Another method has been introduced by Hynes and Martin (1936) which projects the images on to a ground glass screen over the eye-piece with a magnification of two thousand. The cell size is directly measured on this screen, without drawing, by using a celluloid protractor.

It has been known however that the method of using dry films does not give the accurate size of the cell as it exists in the circulation. The cells change readily their shape and size according to the nature of the surrounding medium.

Ponder (1934) in 1922 therefore devised a photographic method with a special camera by which permanent photographs of the cells in plasma and other surroundings can be taken with high magnification. The cell size is determined directly from the plate the magnification having been known by previous graduation.

The method was later developed by Ponder and Millar (1924) and again elaborated further by Dryerre, Millar and Ponder (1926). The effects of various conditions of the plasma by changing its reaction, temperature, CO_2 and oxygen tension, etc., on the size of the cells can thus be studied. According to Ponder (loc. cit.) drying always gives a reading lower by about 15% on an average compared with that obtained in the 'wet' state. There is however no constancy in the amount of shrinkage undergone in any given case.

Ponder's photographic method requires a highly expensive and technical apparatus and is thus not suitable for routine use. Its use is mainly confined to research work.

Of late attempts have been made to devise simple methods for routine clinical use all of which are based on the principle of diffraction and are hence known as the Diffraction Methods.

The diffraction method was first suggested by Young (1813) in 1813 but was never widely used till Pijper (1919) revived it in 1919.

If a bright light is looked at through a film of small circular objects, say a film of blood cells, the light is seen to be surrounded by coloured rings known as the 'halo' the diameter of which varies inversely with the size of the small objects. The coloured rings are due to the diffraction of the light, a breaking up of the light into its spectral components, as it passes against the edges of the small objects. The 'haloes' are calibrated beforehand for different sizes of the red cells and a direct reading

can thus be obtained, or the size of the cell can be calculated from the size of the 'halo' with the aid of mathematical formulae.

There are various kinds of instruments based on this principle and named after their inventors. Thus there is Pijper's or Millar's Diffractometer, Emmon's Eriometer, Eve's Halometer and the more recent Haden-Hausser Erythrocytometer.

Recently Allen and Hanburys, London, have put on the market their Direct Halometer which is both cheap and handy. This has already been described in a previous communication (Telang, 1940). The most common size of the red cells is read directly on the scale graduated on the instrument. The personal error is said to be only $0.2\ \mu$. The size is determined on dried films only. This would no doubt give slightly lower figures as drying leads to some shrinkage in the cells but in clinical practice absolute values are not of primary importance and relative values for the size would serve equally well for diagnostic and therapeutic purposes.

An objection raised against 'halometers' or 'diffractometers' in general is that the reading does not give an idea of the scatter of the size in a film, that is, it is not a measure of the degree of the anisocytosis when it is present. It is however said that by constant practice one may be able to gauge the degree of anisocytosis from the quality of the 'haloes.' Thus the manufacturers of the Direct Halometer claim that anisocytosis should be suspected when the 'haloes' are imperfect and lacking in sharpness.

It has also been said against 'halometry' that it does not give comparable results with the, Price-Jones method of direct measurement. This is however still a controversial point. Thus while Chatterjee (quoted by Bhatia, 1938) says that the camera lucida method and the Halometer give remarkably different results Chaudhuri (1933-34) from statistical considerations opines that 'halometry' is reliable.

RESULTS AND DISCUSSION

The results obtained by an examination of 131 blood films* with the Direct Halometer are given in Table I.

TABLE I

Total number of films=131	
Range	6.4 to 7.75 μ
Mean size $+$ P. E.$_m$	7.021 $\mu \pm$ 0.019
Standard deviation $\pm$ P. E. σ-	0.318 $\pm$ 0.013
Coefficient of variation% $\pm$ P. E.$_{C. V.}$	4.533 $\pm$ 0.1893.

The subjects were medical students between the ages of 18 and 25. The blood was taken directly from the finger without the use of any anticoagulant but with the usual aseptic precautions. Several of the films were repeatedly examined for days together and no noticeable differences were observed in their readings. The statistical constants show that the distribution of the sample is fairly normal.

Price-Jones (quoted by Whitby and Britton, 1937) by his direct method finds the size varying from 4.75 to 9.5 μ in healthy normal men but in more than 90% of cases he finds the range lying between 6.7 and 7.7 μ with a mean of 7.2 μ, standard deviation 0.45 and the c.v. 6%.

Ponder (*loc. cit.*) finds a range from 7.5 to 9.5 μ with the mean at 8.6 $\mu \pm$ 0.3, standard deviation 0.5 and c.v. 5.7% for 'wet' cells measured in plasma and a range of 6.9 to 7.8 μ for 'dry' cells measured in films.

Results obtained by the present writer (Telang, *loc. cit.*) regarding the normal cell size determined with the same instrument but in connection with another investigation gave different figures altogether, *viz.*, mean size 7.75 $\mu \pm$ 0.032, standard deviation 0.26 $\pm$ 0.022 and c. v. 3.3%. The films in that case however were prepared from citrated venous blood.

The difference between this mean figure and the one obtained in the present investigation being statistically significant there must be some cause underlying it. In both the cases the films were prepared and examined under practically identical conditions excepting for two details, *viz.*, (i) the source of blood which was venous and (ii) the presence of the anticoagulant citrate, in the former case. The only way to decide as to which of these two factors may be influencing the size it would be necessary to prepare four films from the same subject, two from the capillary blood and two from the venous blood, one of each with and the other without the addition of the anticoagulant and then to compare the results obtained.

A small number of cases studied from this point indicate the possibility of the anticoagulant being the probable cause rather than the source of

*Kindly provided by Mr. K. M. Moghe, M.B.B.S., of the Histology Department.

the blood but no definite conclusions can be drawn owing to the paucity of the data.

It seems from this that some factors are likely to influence the size of the cell and it would be helpful to consider them.

INFLUENCE OF FACTORS ON THE CELL SIZE

The following factors are said to affect the size of the red cell :

Method used :—As has been mentioned above the source of the blood and the addition of an anticoagulant may affect the reading. It is said that venous blood films give higher readings than films from the finger blood. The use of the anticoagulant also is said to give a higher reading but this is not accepted by all and needs further investigation. The size is also greater when cells are examined in the 'wet' state.

H-ion concentration of blood :—The size is said to vary directly with the hydrogen ion concentration of the blood. Thus cells in venous blood are said to be larger than those in the capillary blood because of the greater H-ion concentration in the former. Price-Jones (1919-20) found the size increasing with the addition of CO_2 to the blood in vitro but Ponder (*loc. cit.*) who has investigated the problem very carefully refutes this statement. He attributes the small difference in the size to the shrinkage undergone by the cells in the preparation of the films as the rate of this shrinking is never constant even in the same person. The same average difference may be noted, he says, in the films prepared from the same blood, arterial or venous, and taken at the same time from the same subject.

Other conditions affecting the H-ion concentration of the blood affect the size accordingly. Thus Price-Jones (1919-20) finds a diurnal variation in the size it being greater in the evening in the same individual (7.5 to 7.6μ) and smaller in the early morning (6.9 to 7.1 μ). He says this is due to the diminution in the alkali reserve of the blood as the day wears on. For the same reason it is said that the size is greater after exercise and less after voluntary ventilation by forced breathing. According to Price-Jones (1919-20) violent exercise (running up and down stairs) causes first an increase in diameter of from 0.16 to 0.46 μ and subsequently a decrease of about the same magnitude while gentle exercise has no effect. Similarly the use of the tourniquet in drawing the blood out is said to increase the size by 0.4 μ.

Ponder (*loc. cit.*) however refutes both the diurnal variation as well as the effect of exercise as also the common belief that arterial and venous blood would show different sizes. He is supported by other workers like Haden (1923) and Wintrobe (1932).

Age :—At birth the mean diameter of the cell is high. Gradually in about two years the normal adult size is stabilised. The course of this stabilisation is however not uniform. Thus Van Creveld (1932) found that in full term born infants there is a gradual fall in the diameter from the third week while in the premature born the decrease in the diameter is more rapid after the third week with a slow rise after the eighth week. At 18 to 20 weeks the size is indistinguishable from that in the full term.

Sex :—No difference has been noted in the cell size in the two sexes.

Race :—A racial difference in the size is suggested by Gram (1884) Thus he found it to be 7 μ in the Italians and 8.5 μ in the Norwegians but others mostly have not found any racial difference. The figures obtained for Indians in this paper do not also suggest any racial difference.

Locality:—It has been found (Ponder, *loc. cit.*) that the same subjects examined in England and in America do not give the same size for their cells hence it is suggested that the locality may have some effect either through its barometric pressure or its humidity etc. or both.

Disease :—As a result of diseased conditions, *e.g.*, in anaemias, the red cell size may be either increased (macrocytic), decreased (microcytic), or unaffected (normocytic). As the causation of these types of anaemias depends upon factors like gastric function, intestinal absorption, diet, storage of haematinic principle by the liver, haemorrhage, sepsis, etc., indirectly the cell size varies with these processes also.

Cell Size in Relation to Haemolysis, Haemoglobin Content and Red Cell Count

As osmotic haemolysis involves initial swelling of the corpuscle before bursting it was investigated statistically (Telang, *loc. cit.*) whether there is any relationship between the size of the cell and its haemolysing property. No such relationship was found. A slight but significant relationship was however found between the size and the haemoglobin content. There was also a significant negative correlation between the size and the red cell count suggesting probably that the total amount of haemoglobin circulating in a given normal individual may be constant.

Summary

(i)   The mean size of the human red cell determined by the examination of blood films from 131 normal adults (age range 18—25) by the Direct Halometer was 7.021 μ + 0.019 with the range from 6.4 to 7.75 μ. The standard deviation and the c. v. per cent. were 0.318 $\pm$ 0 013 and 4.533 $\pm$ 0.1893 respectively.

(ii)   The subject of red cell size is reviewed and the results obtained discussed.

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THE INFLUENCE OF THE CHEMICAL AND THE MICROBIAL AGENCIES IN THE NITROGEN STATUS OF THE SOIL

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THAT the Nitrogen of the soil undergoes fluctuations as a result of "weathering" is a point beyond question. All the references available make mention only of the physical and the chemical agencies bringing about "The Cycle of Weathering in Soil ;" but the idea that micro-organisms may have an important part in the process cannot be ruled out in the present state of microbiological knowledge. In order to determine the relative importance of the two main agencies, *viz.*, the chemical and the microbial, in the process of Nitrogen fluctuations, it occurred to us that it would be possible to reproduce natural conditions of exposure in the laboratory. It was possible to exclude the microbial factor from the soil for a sufficiently long time to obtain detectable results ; but it was not possible to obtain the results of microbial activity without some form of exposure to physical and chemical agents. Since no literature was available dealing with "weathering" of Nitrogen as such, we contented ourselves for the time being in taking the main natural conditions themselves as represented by direct sunlight, diffused sunlight and darkness as the light-weather conditions. Since we were quite aware of the significance of moisture, we controlled the moisture conditions artificially by the addition of ammonia-free sterile distilled water in the soil samples to be exposed under arable conditions. Nitrogen changes were studied under three moisture conditions, *viz.*, (1) soil containing only hygroscopic water, (2) soil containing capillary water, and (3) soil containing hydrostatic water or soil in a water-logged state.

The next point, *viz.*, the way of separating the chemical action from the microbial action did not present any difficulty either. It was possible to study the Nitrogen changes due to chemical agencies alone by excluding the microbial factor by sterilization of the soil ; but in the study of microbial action as we have mentioned before, it was not possible to exclude the chemical agencies. Yet the changes in the non-sterile soil must be naturally due to the combined activity of the chemical and the

microbial agencies, and so the difference between the changes induced by the combined chemical and microbial agencies together on one hand (in the non sterile soil) and the chemical agencies alone on the other (in the sterile soil) would be with good approximation a measure of changes brought about by microbial agencies alone.

EXPERIMENTAL

Apart from the control sets, 36 Eilenmeyer flasks, provided with cotton plugs, and each containing 5 grams of the experimental soil sample were taken and 18 of them were sterilized by autoclaving. Those of the sterilized 18 constituted the "sterile set" and the others constituted the "non-sterile set." Out of each of the two sets ,6 soil samples were rendered in a semi-saturated state by the addition of 3 c.c. of sterile ammonia-free distilled water in each of them, and another series of 6 samples from each set were water-logged by the addition of 25 c.c. of the same water aseptically. Then all the soil samples were exposed to the light-weather conditions mentioned before for 2 months and then the Nitrogen contents—total and soluble—of each sample were determined by the Kjeldahl method ; the values obtained were expressed as so many parts of Nitrogen per million parts of the soil.

As a complementary work to the above, another series of experiments were conducted to find out, if possible, the influence of microbial counts in the Nitrogen status of the soil. This was done with a view in the first place to determine the total number of micro-organisms in the soil, their relative viability in the three moisture states in the soil and under the three different light-weather conditions. These samples were also exposed to the three different light-weather conditions for two months under appropriate moisture states, and their microbial contents were evaluated by culturing and counting the colonies on an improvised synthetic medium. Although a complete significance of the counts obtained on the Nitrogen changes cannot be fully explained in absence of the differential counts and other valuable data, the work proved itself to be valuable in visualizing the influence of microbial action on this important phenomenon of soil, viz., its Nitrogen status.

The following table will show the losses recorded in the total and the soluble Nitrogen in each of the differently treated soil samples ; the microbial populations of the soil samples after the exposure has been affected (2 months) are indicated against each of the samples.

1. DIRECT LIGHT

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	Non-sterile set		Sterile set		Microbial count
	Total	Soluble	Total	Soluble	
Dry	432.64	276.00	158.36	41.44	1,052,083
Semi-saturated	398.72	258.88	189.32	20.72	2,000,000
Water-logged	263.68	180.32	96.28	55.44	1,835,600

2. DIFFUSED LIGHT

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	Non-sterile set		Sterile set		Microbial count
	Total	Soluble	Total	Soluble	
Dry	1025.64	154.88	256.40	86.04	1,406,250
Semi-saturated	432.64	62.94	78.44	41.44	1,968,750
Water-logged	510.60	441.92	196.28	34.44	2,670,000

3. DARKNESS

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	Non-sterile set		Sterile set		Microbial count
	Total	Soluble	Total	Soluble	
Dry	277 20	138 88	107.16	20.72	1,312,500
Semi-saturated	449 48	166.60	196 28	43 16	1,875,000
Water-logged	474 08	258.88	189 32	23 36	3,192,000

CONCLUSION

The losses indicated in the non-sterile samples in all the cases are greater than the losses shown in the sterile samples. The losses in the non-sterile are as a result of the action of the combined chemical and microbial agencies; in the sterile the action is due to only the chemical agencies. So, if the losses indicated in the sterile samples be deducted from the losses observed in the corresponding non-sterile samples, the difference obtained will be the losses that have occurred in the soil-Nitrogen as a result of Microbial agencies alone.

From the above results the main conclusions we draw may be summarized as follows :—

1. Under all conditions of light-weather, loss in Nitrogen occurs more rapidly as a result of the microbial action rather than that of the chemical action. It is also observable that the loss in the non-sterile sample under diffused light is the maximum and this is attributable to ammonification in the soil brought about by the microbial factor. So, also, the loss in the soluble is at its maximum in the water-logged state of the soil under diffused light and this loss is attributable to denitrification process which is made possible here by the anaerobiosis afforded by water-logging.

2. The presence of moisture to the extent of semi-saturation in the soil helps in the checking of nitrogenous losses despite its affording greater possibilities for the gases of the atmosphere to cause more extensive losses in Nitrogen.

3. Direct sunlight appears to bring about greater losses in the so-luble Nitrogen contents of the soil, especially when the soil is non-sterile.

4. Direct sunlight shows an inhibitory action on the growth of micro-organisms as may be judged from their counts.

THE DAILY RATE OF LOSS IN SOIL NITROGEN CONTENTS

By

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IT was observed that the soil under certain conditions undergoes losses in its Nitrogen contents which are not only detectable but are actually measurable daily. In other words, it is possible to determine the daily rate of loss of soil Nitrogen, and for this loss to occur the soil must be in small quantities and exposed under diffused light. For measuring the losses in the total Nitrogen, a dry sample of the soil affords ideal conditions ; and, for the water soluble Nitrogen, a water-logged state of the soil under the same light-weather affords better conditions.

Experimental.—14 Erlenmeyer flasks, each containing 5 grams of the soil were employed ; 7 of them were meant for estimating the total Nitrogen contents and the other 7 for the water soluble Nitrogen : The former set was maintained in the air-dried state of the soil and the latter set was water-logged with 25 ç.c. of ammonia-free distilled water in each sample. The Nitrogen contents were determined after one day, two days, three days, four days, five days and six days, respectively. The results given below are for the total Nitrogen contents.

TABLE 1

TOTAL NITROGEN VALUES

	Time of Exposure	N. in parts per million parts
1	Control	1879.08
2	After 1 day of exposure	1740.48
3	,, 2 days ,,	1658.32
4	,, 3 ,, ,,	1601.88
5	,, 4 ,, ,,	1571.36
6	,, 5 ,, ,,	1546.44
7	,, 6 ,, ,,	1518.72

It is evident from the above results that the loss in the total Nitrogen is at its maximum in the first 24 hours of exposure and thereafter there is a progressive decrease in the rate of loss of Nitrogen corresponding to the diminution in the total amount of Nitrogen in the samples. In fact, the loss between the 5th and 6th days équals only about one-fifth of the total loss that has occurred within the first 24 hours of exposure and correspondingly the total Nitrogen has also decreased by about one-fifth of the total Nitrogen initially present in the soil : In other words, it appears that the evolution of Nitrogen is more active when a comparatively large amount of Nitrogen is present in the soil and that the depleted soil seems to develop an increased strength of retentive power as the total Nitrogen decreases. It may be that this gradual decrease may go on for a very long time until the end-point of "weathering" in Nitrogen is reached.

Under the water-logged state, the soil shows a measurable decrease in soluble Nitrogen ; this decrease is attributable to the denitrification process (unlike the loss in the previous instance which is attributable to ammonification) which is made possible here by the anaerobic condition afforded by water-logging. The results obtained were as follows :

TABLE 2

SOLUBLE NITROGEN VALUES

	Time of Exposure	N. in parts per million parts
1	Control	520.80
2	After 1 day of exposure	409.64
3	,, 2 days ,,	354.20
4	,, 3 ,, ,,	316.48
5	,, 4 ,, ,,	283.32
6	,, 5 ,, ,,	260.12
7	,, 6 ,, ,,	247.40

From the above results it becomes evident that just as in the case of the total Nitrogen losses, the loss in the soluble Nitrogen is maximum after the first 24 hours of exposure and that thereafter there is a gradual decrease commensurate with the decrease in the amount of soluble Nitrogen.

THE DAILY RATE OF LOSS IN SOIL NITROGEN CONTENTS

A-B = TOTAL NITROGEN VALUES

C-D = SOLUBLE NITROGEN VALUES
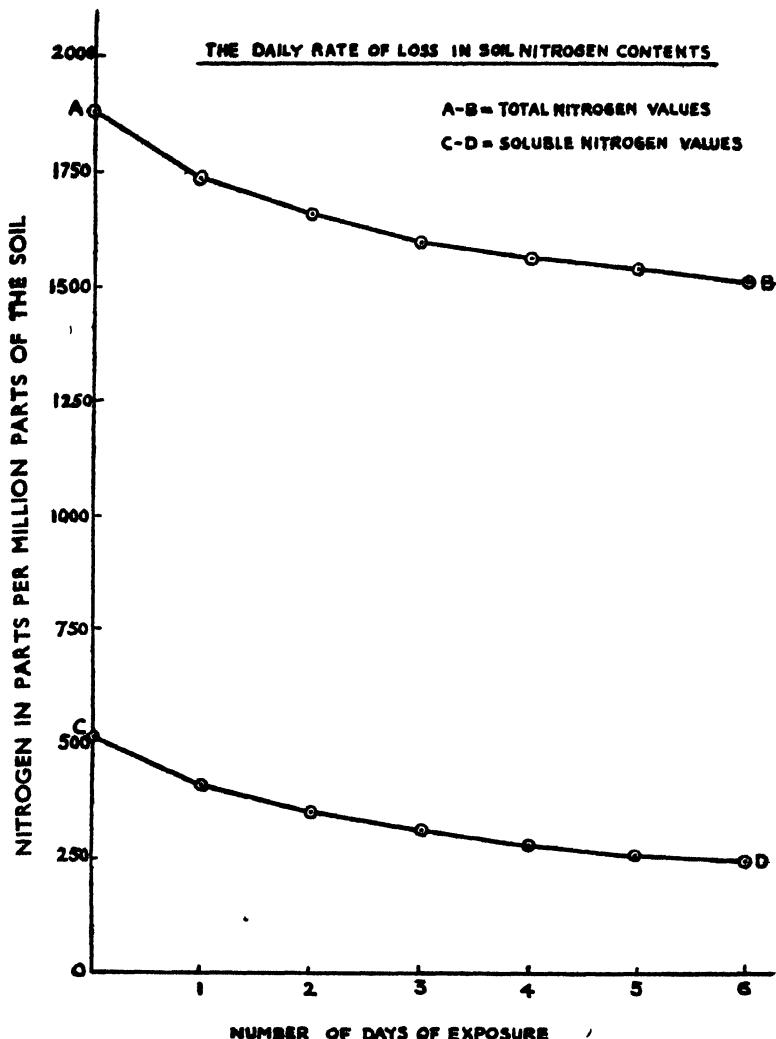
A NOTE ON THE COLD STORAGE STUDIES OF LITCHI FRUIT (NEPHELIUM LITCHI)

By

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AND

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THE litchi fruit is a native of South China where it grows abundantly and is canned for export purposes. Its introduction into India, Ceylon and the West Indies in the tropics is of recent origin. It is believed that it was introduced into Bengal at the end of the 18th century (Popenoe, 1930).

In some parts of India, litchi is prized next to mango. It is principally grown in Nadia, Berhampore, Hooghly Rajashahi and Malda in the Province of Bengal and Saharanpur, Dehra Dun, Fyzabad, Azamgarh, Balia and Gorakhpura in the United Provinces. It is also grown on a large scale in the Province of Bihar. There are a number of varieties of litchi such as Early Bedana, Early Large Red, Calcuttia, Sahi, Late Bedana, Bombai and Deshi. The fruit is sold from annas three to annas eight per seer (2 lbs.) in Bengal and from annas eight to one rupee eight annas per 100 fruits in the United Provinces. These prices clearly show that it is a money crop. Statistics relating to acreage and volume of trade in litchi are not available. During recent years some plantations have also been laid out in the southern part of the Surat district in the Bombay Province.

The ripe litchi fruit has an outer shell-like covering having a brilliant red colour. The flesh within this tough outer covering is white and has the consistency of a Muscat grape. An analysis of the fresh fruit made in Hawaii (Higgins, 1917) showed that the flesh contained 20.92 solids, 0.54% ash, 1.16% acids, 1.15% protein and 15.3% total sugars. In another analysis it was found that the seeds constituted 17.03%, the skin or shell 7.86% and the flesh 75.1% of the weight of the fruit. Of the various Indian foodstuffs investigated by Ghosh and Guha (1925), litchi appears to be one of the richest sources of vitamin C. An analysis of the fruit used by the authors of this note for the cold storage trials reported later showed that seeds constituted 25%, skin 8% and pulp or flesh 67% of the total weight of the fruit.

The litchi fruit loses its attractive market appearance when the bright colour of the shell is lost. It is really important to preserve the colour of the shell in order to realize the full value of the fruit. In experiments carried out by Higgins (1917) it was found possible to keep litchi in distilled water for about two weeks with only slight deterioration in appearance and flavour. In the opinion of the above investigator, refrigeration furnishes the best means of preserving the litchi fruit for a limited period in its natural state.

McGuire (1939) has reported that fresh fruit kept quite well at ordinary temperature for two to three weeks without deterioration in flavour, although the attractive red colour of the fruit was lost. Refrigerated fruit, on the other hand, showed no loss in colour or flavour during storage for a fortnight and a transport temperature of about 40-45°F. was recommended for experimental shipments.

Boyes and others (1933) have reported that small quantities of litchi exported from South Africa met with a ready demand at very remunerative prices but the wastage was extensive. In view of the lack of information regarding storage requirements of litchi, cold storage trials of the fruit were undertaken. Fruit from three successive pickings were stored for a period of three weeks at 31°, 34°, 37°, and 40°F. The fruit of the first picking which was slightly less mature than the normally picked fruit withstood cold storage temperatures remarkably well. The fruit, remained in good condition for 25 days after removal from the cold storage. This fruit, however, was very tart and lacked flavour when placed in the cold storage and remained in the same condition throughout its storage period. The fruit of the second or mid-season picking remained in cold storage very well, particularly at 31°F and 34°F. The flavour of the fruit was excellent at all the temperatures. The fruit of the third or late season picking proved unsatisfactory at all the storage temperatures employed. The fruit developed surface mould at higher temperatures but there was an internal breakdown at all the storage temperatures. The authors concluded that litchi did not ripen to any appreciable extent in cold storage. They, therefore, recommended that the fruit intended for cold storage should be picked as soon as it acquired its characteristic aroma and bouquet.

It is principally on account of its trade importance in the United Provinces, Bengal and Bihar and export possibilities that a cold storage trial of litchi was included in the programme of the Cold Storage Research Scheme, Kirkee. In 1937, ripe litchi fruit of the Sahi variety was obtained from Muzaffarpur in the Bihar province for a preliminary cold storage trial. The fruit was brought in bamboo baskets as well as in a refrigerated container. There was comparatively little loss in transit in fruit which was brought in the refrigerated container. The fruit was sorted and the sound fruit placed in the chambers at 30°, 35°, and 40°F. It was observed that the red colour of the fruit gradually turned brown in storage at the above temperatures and the shell became more tough and could be easily separated from the translucent pulp. The change of colour was more rapid at 40°F than at 30° and 35°F, and at the latter temperatures the shell of the fruit retained its red colour for about a week only. The change of colour of the shell, however, affected only the outward appearance of the fruit and had no bad effect

on the pulp. At all the above three temperatures the fruit remained in good condition for about two months (Plate I).

The effect of wrapping the fruit in wax paper and giving a thin coating of paraffin wax on the shell was also investigated. It was observed that in both the treatments the bright red colour of the shell turned brown. The question of the preservation of red colour of the shell of litchi is, however, so vital in fruit trade that further investigation is considered essential.

The rate of loss in weight during storage at different temperatures of unwrapped fruit and of fruit wrapped in wax paper was determined. The rate of loss in weight of the fruit wrapped in wax paper was less than that of the unwrapped fruit. For the first four weeks of storage, the rate of loss in weight was practically the same at the three storage temperatures.

TABLE I

Rate of loss in weight of litchi during storage

(PERCENTAGE LOSS IN WEIGHT)

No. of days of storage	32°F.		35°F.		40°F.	
	Unwrapped	Wrapped in wax paper	Unwrapped	Wrapped in wax paper	Unwrapped	Wrapped in wax paper
8	6.8	2.8	6.2	2.7	6.4	3.0
15	8.6	4.5	8.9	4.6	8.4	5.3
22	10.0	6.3	10.8	5.9	10.6	7.3
29	11.9	8.2	12.7	7.2	12.7	8.8
36	13.5	10.1	14.6	8.4	14.7	10.4
50	16.3	13.5	19.0	11.8	19.7	15.7
64	19.3	16.9	23.1	15.2	25.1	22.1

SUMMARY

The results of a preliminary cold storage trial of the litchi fruit carried out at the Cold Storage Research Scheme, Kirkee, financed by the Imperial Council of Agricultural Research, show that it is possible to keep ripe litchi fruit in sound condition for about two months at 30°, 35°, and 40°F. The red colour of the outer shell, however, turns brown during storage. If cold storage is not found useful for fresh fruit trade, it is felt that facilities for cold storage will be advantageous in promoting the trade in canned litchi.

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Plate I   Litchi fruit after two months storage at 35°F

A CASE OF CLEFT STERNUM (SCHISOSTERNIA) IN A FULL TERM HUMAN FOETUS

By

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THE presence of Cleft Sternum is of very rare occurrence. During my experience of the last 13 years in the Anatomy Department of the Grant Medical College, Bombay, and the King Edward Hospital Medical School, Indore, while more than 500 bodies have been dissected, I have not come across a condition similar to that noted in this case, although similar cases have been recorded in the literature.

The specimen under review was sent to this department from the B. J. Hospital for Children through the Pathology Department of the College. The records of the case showed that the subject was a Hindu female, full-term, weighing 6 lbs., born in Bai Motlibai Obstetric Hospital, with a pulsatile cystic swelling over the precordium. The baby was immediately transferred to the B. J. Hospital for further investigation and treatment of the swelling. She, however, died within four days after birth.

The body was dissected and the following abnormal features were noted :—

The skin over the front of the trunk was unbroken, but relatively thin, and that over the precordium covered a slight ventral bulging. On reflection of the skin and fatty superficial fascia over the front of the whole trunk, the white membranous deep fascia was exposed, extending from the lower margin of the mandible above to the symphysis pubis below. In the cervical region, it was of moderate thickness and covered the soft structures of that region including the thymus. In the lower part, however, a white median vertical thickened band between the sternal ends of the clavicles could be distinctly differentiated from the rest of the membranous deep fascia. In the thoracic region, the deep fascia stretched as a thin membrane between the two separate vertical sternal bars, to the margins of which it was firmly attached. Lateral to that attachment it covered the great pectoral muscle on either side. Deep to the membranous layer was exposed the pericardium to which

it was connected by strands of loose cellular tissue. The pericardium presented an unbroken membrane as it surrounded the heart within. In the median plane of the abdominal region, the deep fascia appeared as a thin white membrane stretching between the medial margins of the widely separated recti abdominis muscles upto a level midway between the umbilicus and the symphysis pubis, below which these two muscles remained approximated. Laterally, on each side, the membranous deep fascia was continuous as (i) the anterior wall of the rectus sheath, and (ii) a thin layer covering the posterior surface of the rectus abdominis (in the same plane as the transversalis fascia of the adult). Deep to it was placed the parietal peritoneum.

The clavicle and sterno-clavicular joint showed normal development on each side. The sternum was deficient in its normal position in the median plane and was present in the form of two halves, consisting of hemimanubria and hemisternebrae, separated from each other by a wide interval,......the sternal fissure. Exposed in the fissure were the heart and pericardium covered by skin and fascia only. (An exposed position of the heart and pericardium is described as "ectopia cordis"). The hemimanubria and the upper three hemisternebrae of the cleft sternum showed normal osseous development. Twelve pairs of ribs were normally developed and showed on either side the normal connections with the corresponding half of the cleft sternum by costal cartilages.

The pericardial and the two pleural cavities were completely separated from the peritoneal cavity by the diaphragm, the anterior margin of which was clearly developed between the pericardial and peritoneal cavities, and was attached to the deep surface of the white membranous deep fascia that stretched between the margins of the sternal fissure and the medial margins of the widely separated recti abdominis muscles. In the cleft of the anterior abdominal wall between the medial margins of the recti abdominis were exposed, beneath the parietal peritoneum, a part of the liver, a part of the pyloric region of the stomach, and the left umbilical vein ascending from the umbilicus to the cleft between the right and left lobes of the liver. The whole intestinal tract was normally developed and was in its normal place in the abdominal cavity.

In the same specimen there was a developmental anomaly of the Right Subclavian Artery. The artery originated from the termination of the Arch of the Aorta immediately to the left of the vertebral column, from where it extended upwards and to the right through the superior mediastinum, crossing in front of the vertebral column and behind the oesophagus, and finally left the thoracic inlet to enter the right side of the root of the neck whence it followed its normal course. The innominate artery continued as the right common carotid artery in the neck.

EMBRYOLOGICAL EXPLANATION OF THE ANOMALIES

The comparative anatomy and phylogeny of the sternum reveals that it is a structure which is developed partially among the fishes, but reaches a higher type of construction and greater importance in the amphibia and reptiles. It, however, presents a simple form among

Fig. 1

Superficial dissection of the anterior
aspect of the Trunk

Fig. 2

Deep dissection of the anterior aspect
of the Trunk

the mammals, becoming flat and considerably modified with the adaptation to the upright posture in man. The sternum originates, in all classes of vertebrates, from two condensed mesodermal plates or sternal bars, which are at first situated in the lateral part of the body-wall, being widely separated from each other, by the large heart and liver of the embryo. These mesodermal sternal bars subsequently become chondrified, and, having moved towards the precardial region, fuse with each other cranio-caudally in the mid-ventral line to form a median cartilaginous plate. The "episternal structures," *viz.*, the epicoracoid cartilages of the pectoral girdles and the membranous interclavicle may participate in the formation of the presternum (*i.e.*, the first piece of the sternum), but the extent to which they enter into its formation diminishes in ascending from the lower to the higher types of vertebrates. The human manubrium thus appears from its development to be a compound of several embryonic elements, a fact supported by multiple centres of ossification which appear in this part of the developing sternum. The mesodermal sternal bars and the "episternal structures" originate independently of the ribs.

In the study of the present specimen, the origin of the anomaly of the "cleft sternum" seems to have occurred during the chondrogenous stage in the development of the sternum. The anomaly appears to be the result of failure of the double cartilaginous hemisternum to coalesce, but the osseous development of each cartilaginous hemisternum has progressed in the normal manner, resulting in the formation of two hemimanubria and hemisternebrae separated from each other by a wide fissure. The separation of the cartilaginous sternal bars does not represent an ancestral phase in the phylogeny of the sternum, but has occurred during its ontogeny to accommodate first the yolk-sac and later the large heart and liver of the embryo

The white membranous deep fascia, which stretches between the sternal bars as well as between the medial margins of the recti abdominis muscles, represents the persistence of the "primitive linea alba." It is not only wide but also extends from the neck to the perineum during the early stages of development.

The abnormal origin and course of the Right Subclavian Artery, seen in the same specimen, is the result of persistence of the right dorsal aorta caudal to the level of origin of the 7th right intersegmental artery from it together with the disappearance of the right 4th aortic arch and the part of the right dorsal aorta cephalic to the origin of the same intersegmental artery. This anomaly of the artery, however, bears no relation to the Cleft Sternum.

The two photographs (Figs. 1 and 2) show the superficial and deep dissection of the anterior aspect of the trunk respectively.

TWO NEW SPECIES OF ASPIROMITUS ST. FROM BOR GHAT (LONAVLA AND KHANDALA)

By

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AND

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WHILE the junior author was working on Anthoceros from Poona and neighbouring places on the hills of the Western Ghats he collected the following two forms from Anthocerotaceae. From the general appearance the forms appeared to be interesting and so we undertook to work out these forms from taxonomical point of view   On consulting Dr. S. K. Pande of Lucknow it was found that the specimens belonged to the Genus *Aspiromitus St.* This paper gives an account of these forms which are quite new.

Aspiromitus khandalensis, sp. nov.   (Pl. I;   Figs. 9)

This form is found on compact soil on nearly level, shady ground, foot-paths in fields, road sides, large flat grounds surrounding the bunglows, etc., at Lonavla.   Plants with ripe capsules were collected during the third week of September.

The plants are large and circular with a diameter of 40 mm. in some cases, and are firmly attached to the soil.   They are dark green in colour, blackening with age.   Segments are dichotomous, oblong or wedge-shaped, prostrate, slightly ascending at the free ends, at first radiating, later becoming somewhat entangled owing to the overlapping of the segments.   The thallus is cavernous and contains large mucilaginous cavities and nostoc colonies.   Under a lens the thallus shows the charateristic polygonal areas, which represent the internal cavities marked out by a net-work of dark lines.   The surface cells are rectangular or polygonal having practically the same length and breadth which   measure   about   28 μ.   The   thallus   is   15-20   cells thick in the centre.   The margin of the thallus is crisped.   The plants are dioecious.   The female plant bears a large number of capsules.   In one specimen as many as 75 capsules were counted on a

single thallus. The capsules are situated more towards the margin and they go out obliquely. They are about 40 mm. long with stomatal structures on them. Involucres are 4-5 mm. in length, solitary or some times fused in twos or threes. The stoma with its guard cells measures 56 μ × 35 μ. The spores are dark black and measure upto 60 μ in diameter. The surface is studded with blunt spines. The elaters are many-celled, short, bent and at times branched.

The male plants which are closely associated with the female plants are smaller in size. They are circular in form and unlike the female plants are deeply lobed. The plant size varies greatly. The biggest plant collected has a diameter of 20 mm while the majority of plants are about 10 mm. in diameter. In a large number of cases the central part of the thallus decays soon and the lobes get separated. Each lobe is long and narrow and shows dichotomous branching. The segments are short, broad and wedge-shaped. Like the female plant the thallus shows the characteristic polygonal areas marked out by the network of dark lines. These are very prominently seen on the raised up portions of the thallus towards the margin. In the mature specimen the upper surface of the thallus is studded with yellow dots representing the antheridial chambers. Each antheridial chamber is a very big cavity and contains a large number of antheridia. In one specimen as many as 30 antheridia were counted. Each antheridium has a long stalk and it measures 175 μ × 91 μ.

Aspiromitus Fergussoni, sp. nov. (Pl. II; Figs. 10)

This form is found at Lonavla. It grows on soft lumps of soil under hedges, or on compound walls which are under thick shade of large trees. It is found during the months of August and September.

Plants are found in dense clusters. They are dioecious. The male and female plants are closely associated with each other. The size of the plant varies greatly. In big female plants the thallus has a diameter more than 45 mm. The thallus is a rosette with four or five, rarely more, deep lobes slightly overlapping. The lobes are sub-erect or sometimes prostrate. In old plants the central part decays and the lobes get separated. Each lobe has a truncate form and is from 15 to 20 mm. in length. When seen under a lens the thallus shows oblong or polygonal areas marked out by dark lines. These areas represent the cavities present in the thallus. The thallus is cavernous and light green in colour. The surface cells are closely packed together and are rectangular or polygonal in shape. They measure 35μ-42μ×49μ-63μ. Capsules arise from near the margin and are about 40 mm. rarely 50 mm. long. On a single thallus 20 to 40 capsules are developed. They are stomatiferous. Each stoma with the guard cells measures 63μ×42μ. The involucres are 7 mm. long, solitary or fused in twos or threes. At the apex it consists of a brownish membranous sheath with a toothed margin. Spores are dark black in colour and have a spiny surface. The spines are pointed. They measure 36μ-40μ in diameter. The elaters are very peculiar. They are mostly multicellular, straight and extremely elongated. Some of them are, however, short, bent and with or without lateral short branches.

The structure and the form of the male plants are like those of the female ones except that they are much smaller and more erect. The upper portions of the erect lobes, in mature specimens, are studded with large yellow antheridial chambers which are seen even from a distance. Each chamber contains a very large number of antheridia, generally 40 but in one specimen as many as 100 were counted. The antheridium is large and has a short stalk. The antheridium measures 160 μ × 100 μ. The antheridia in a bunch are of various sizes and they do not ripen simultaneously.

IDENTIFICATION

From the nature of the antheridium it can be easily seen that these forms are of *Aspiromitus St.* and not of *Anthoceros Linn.* Both the forms are dioecious and naturally only need be compared with the four dioecious forms out of 55 species described by Stephani, (1) of which—*A. expansus* and *A. dioicus St.* only have dark spores. In *A. khandalensis* the size of the spore is 60 μ as against 36 μ in these two species and therefore it is described as a new species and the name given to it is after the locality where it was first found.

A. Fergussoni St. closely agrees with *A. dioicus St.*, in the size and structure of the spore but the latter differs greatly in having only 3-5 antheridia in a chamber while in the former they are innumerable—generally 40. It also differs from *A. expansus St.*, in the length of the capsule and the structure of the spore. Therefore it has also been described as a new species and is named after the College in which the work has been carried out.

Both these forms being dioecious need no comparison with *A. manglo-reus St.*, which is monoecious.

After this paper was sent for publication a note on *Aspiromitus St.*, from Khandala was published by Dr. T. S. Mahabale (2) of Ahmedabad describing a new species of *Aspiromitus St.* which he has named *A. Dixitianus.* The two species described above are quite different from the one described by Mahabale and the authors have published a short note on them (3). *A. khandalensis* has a circular thallus, capsules up to 40 mm., spores 60 μ in diameter and the antheridium 175 μ × 91 μ as against the thallus not circular, capsules up to 20 mm., spores 40 μ in diameter and antheridium 34 μ in length. Similarly *A. Fergussoni* differs from *A. Dixitianus* in having a circular lobed thallus, longer involucre, much longer capsules and far bigger antheridia both in number and size.

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EXPLANATIONS OF PLATES

PLATE I

ASPIROMITUS KHANDALENSIS, SP. NOV.

Figs.—1. Plant with sporogonia ; 2. Part of the plant magnified ; 3. Male plant showing antheridial chambers ; 4. T. S. of the thallus—only in part ; 5. Stoma from the capsule ; 6. T. S. of the involucre—only in part ; 7. Surface cells from the dorsal side of the thallus ; 8. Bunch of antheridia—only in part 9. Spore with elaters.

PLATE II

ASPIROMITUS FERGUSSONI, SP. NOV.

Figs.—1. Male plant showing antheridia ; 2. A segment of a male plant ; 3. Female plant with sporogonia about ½ part ; 4. T. S. of the thallus—only in part ; 5. Stoma from the capsule ; 6. T. S. of the involucre—only in part ; 7. Surface cells from the dorsal side of the thallus ; 8. Antheridia ; 9. Spore with elater ; 10. Microphotograph of Spores and elaters. (Elaters seen in parts).

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The plants are large and circular with a diameter of 40 mm. in some cases, and are firmly attached to the soil.   They are dark green in colour, blackening with age.   Segments are dichotomous, oblong or wedge-shaped, prostrate, slightly ascending at the free ends, at first radiating, later becoming somewhat entangled owing to the overlapping of the segments.   The thallus is cavernous and contains large mucilaginous cavities and nostoc colonies.   Under a lens the thallus shows the charateristic polygonal areas, which represent the internal cavities marked out by a net-work of dark lines.   The surface cells are rectangular or polygonal having practically the same length and breadth which   measure   about   28 μ.   The   thallus   is   15-20   cells thick   in   the   centre.   The   margin   of   the   thallus   is   crisped.   The plants   are   dioecious.   The   female   plant   bears   a   large   number   of capsules.   In one specimen as many as 75 capsules were counted on a

single thallus. The capsules are situated more towards the margin and they go out obliquely. They are about 40 mm. long with stomatal structures on them. Involucres are 4-5 mm. in length, solitary or some times fused in twos or threes. The stoma with its guard cells measures 56 μ × 35 μ. The spores are dark black and measure upto 60 μ in diameter. The surface is studded with blunt spines. The elaters are many-celled, short, bent and at times branched.

The male plants which are closely associated with the female plants are smaller in size. They are circular in form and unlike the female plants are deeply lobed. The plant size varies greatly. The biggest plant collected has a diameter of 20 mm while the majority of plants are about 10 mm. in diameter. In a large number of cases the central part of the thallus decays soon and the lobes get separated. Each lobe is long and narrow and shows dichotomous branching. The segments are short, broad and wedge-shaped. Like the female plant the thallus shows the characteristic polygonal areas marked out by the network of dark lines. These are very prominently seen on the raised up portions of the thallus towards the margin. In the mature specimen the upper surface of the thallus is studded with yellow dots representing the antheridial chambers. Each antheridial chamber is a very big cavity and contains a large number of antheridia. In one specimen as many as 30 antheridia were counted. Each antheridium has a long stalk and it measures 175 μ × 91 μ.

Aspiromitus Fergussoni, sp. nov. (Pl. II; Figs. 10)

This form is found at Lonavla. It grows on soft lumps of soil under hedges, or on compound walls which are under thick shade of large trees. It is found during the months of August and September.

Plants are found in dense clusters. They are dioecious. The male and female plants are closely associated with each other. The size of the plant varies greatly. In big female plants the thallus has a diameter more than 45 mm. The thallus is a rosette with four or five, rarely more, deep lobes slightly overlapping. The lobes are sub-erect or sometimes prostrate. In old plants the central part decays and the lobes get separated. Each lobe has a truncate form and is from 15 to 20 mm. in length. When seen under a lens the thallus shows oblong or polygonal areas marked out by dark lines. These areas represent the cavities present in the thallus. The thallus is cavernous and light green in colour. The surface cells are closely packed together and are rectangular or polygonal in shape. They measure 35μ-42μ × 49μ-63μ. Capsules arise from near the margin and are about 40 mm. rarely 50 mm. long. On a single thallus 20 to 40 capsules are developed. They are stomatiferous. Each stoma with the guard cells measures 63μ × 42μ. The involucres are 7 mm long, solitary or fused in twos or threes. At the apex it consists of a brownish membranous sheath with a toothed margin. Spores are dark black in colour and have a spiny surface. The spines are pointed. They measure 36μ-40μ in diameter. The elaters are very peculiar. They are mostly multicellular, straight and extremely elongated. Some of them are, however, short, bent and with or without lateral short branches.

The structure and the form of the male plants are like those of the female ones except that they are much smaller and more erect. The upper portions of the erect lobes, in mature specimens, are studded with large yellow antheridial chambers which are seen even from a distance. Each chamber contains a very large number of antheridia, generally 40 but in one specimen as many as 100 were counted. The antheridium is large and has a short stalk. The antheridium measures 160 μ × 100 μ. The antheridia in a bunch are of various sizes and they do not ripen simultaneously.

IDENTIFICATION

From the nature of the antheridium it can be easily seen that these forms are of *Aspiromitus St.* and not of *Anthoceros Linn.* Both the forms are dioecious and naturally only need be compared with the four dioecious forms out of 55 species described by Stephani, (1) of which—*A. expansus* and *A. dioicus St.* only have dark spores. In *A. khandalensis* the size of the spore is 60 μ as against 36 μ in these two species and therefore it is described as a new species and the name given to it is after the locality where it was first found.

A. Fergussoni St. closely agrees with *A. dioicus St.*, in the size and structure of the spore but the latter differs greatly in having only 3-5 antheridia in a chamber while in the former they are innumerable—generally 40. It also differs from *A. expansus St.*, in the length of the capsule and the structure of the spore. Therefore it has also been described as a new species and is named after the College in which the work has been carried out.

Both these forms being dioecious need no comparison with *A. mangloreus St.*, which is monoecious.

After this paper was sent for publication a note on *Aspiromitus St.*, from Khandala was published by Dr. T. S. Mahabale (2) of Ahmedabad describing a new species of *Aspiromitus St.* which he has named *A. Dixitianus.* The two species described above are quite different from the one described by Mahabale and the authors have published a short note on them (3). *A. khandalensis* has a circular thallus, capsules up to 40 mm., spores 60 μ in diameter and the antheridium 175 μ × 91 μ as against the thallus not circular, capsules up to 20 mm., spores 40 μ in diameter and antheridium 34 μ in length. Similarly *A. Fergussoni* differs from *A. Dixitianus* in having a circular lobed thallus, longer involucre, much longer capsules and far bigger antheridia both in number and size.

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EXPLANATIONS OF PLATES

PLATE I

ASPIROMITUS KHANDALENSIS, SP. NOV.

Figs.—1. Plant with sporogonia ; 2. Part of the plant magnified ; 3. Male plant showing antheridial chambers ; 4. T. S. of the thallus—only in part ; 5. Stoma from the capsule ; 6. T. S. of the involucre—only in part ; 7. Surface cells from the dorsal side of the thallus ; 8. Bunch of antheridia—only in part 9. Spore with elaters.

PLATE II

ASPIROMITUS FERGUSSONI, SP. NOV.

Figs.—1. Male plant showing antheridia ; 2. A segment of a male plant ; 3. Female plant with sporogonia about ½ part ; 4. T S. of the thallus—only in part ; 5. Stoma from the capsule ; 6. T. S. of the involucre—only in part ; 7. Surface cells from the dorsal side of the thallus ; 8. Antheridia ; 9. Spore with elater ; 10. Microphotograph of Spores and elaters. (Elaters seen in parts).

Fig. 1 ×⅔

Fig. 2 ×1

Fig. 3 ×1

Fig. 4 ×57

Fig. 5 ×27
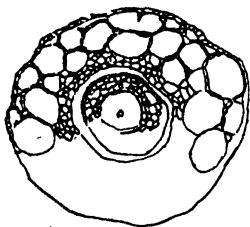
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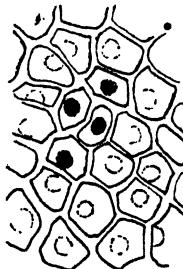
Fig. 7 ×240

Fig. 8 ×100
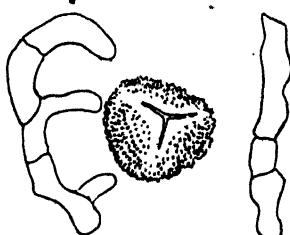
Fig. 9 ×250

Plate I—Figs. 1-9: Aspiromitus khandalensis

Fig. 1 ×2

Fig. 2
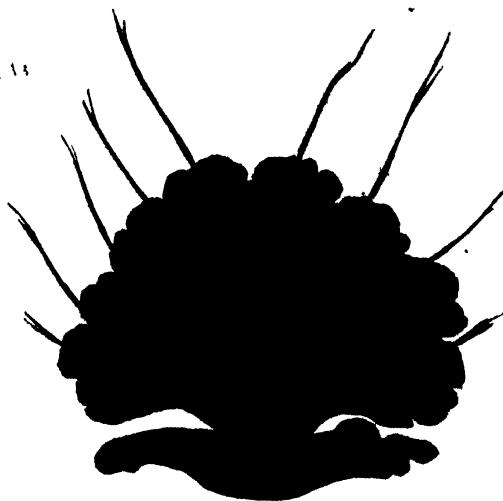
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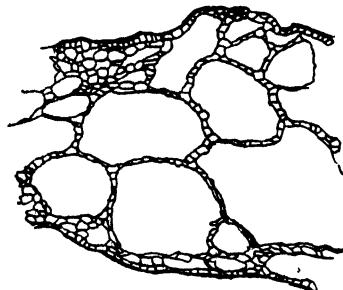
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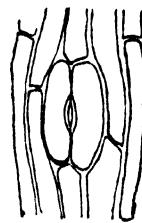
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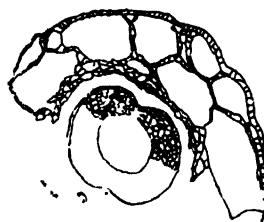
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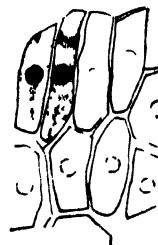
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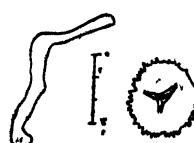
Fig. 8 ×60   Fig. 9   Fig. 10

Plate II—Figs. 1-10 : Aspiromitus Fergussoni

OBSERVATIONS ON SOME SPECIES OF ANTHOCEROS LINN. FROM POONA AND THE NEIGHBOURING HILLS OF THE WESTERN GHATS

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INTRODUCTION

KHANNA (1936) has taken a brief survey of all the species of Antho-ceros Linn. that have been reported from India. In all there are 24 species recorded so far and of these, 16 have been described by Stephani (1912-25) and three by Kashyap (1929). Khanna has added five more very recently. Of these species only one is reported from Bor Ghat—a locality on the Western Ghats. Professors. D. L. Dixit and V. V. Apte during their visits to places on the Western Ghats like Bheemashankar, Lonavla, Mahabaleshwar, etc., observed that these places are exceptionally rich in Anthocerotaceae though they are not so in Liverworts in general, and that more than one species of Anthoceros occur in these localities. It was at their suggestion that this critical taxonomical study was undertaken and the results are incorporated in this paper.

Stephani has described 161 species of Anthoceros Linn. distributed all over the world. The specific characters that he has taken for classification are mainly (i) the nature of the thallus—cavernous or solid, (ii) length of the involucre and its nature—solitary or fused, (iii) length of the capsule, (iv) the size and colour of the spore and the structure of its wall, (v) the sexuality of the plant—monoecious, dioecious, etc., and (vi) the number of antheridia in each chamber. Khanna looks upon epidermal cells also as of diagnostic importance. He has prepared comparative charts giving the characteristics of (i) all the Indian species noted so far, (ii) all the world species with cavernous thallus and black spores and (iii) all the world species with solid thallus and pale spores Kashyap's work on the Liverworts of the Western Himalayas and the papers published on the Indian Anthoceros by Khanna (1932, 33, 37 & 38) have been consulted. In spite of the fact that a number of important differences in some of the forms described here have been noted, the final

identification of some is postponed as the writer fully realises the import-
ance of comparing the new forms with the already established type speci-
mens and as he also feels that a study of the effect of environment on the
morphological characters and also the chromosome number would
possibly help considerably in arriving at the final identification.

Anthoceros sahyadrensis sp. nov. (Pl. I; Figs. 7)

This form is collected from Lonavla. It grows on the large extensive
flat rocky grounds and by the sides of the roads and foot-paths from where
the water is immediately drained off. This form is first to appear soon
after the rains set in and is generally found from the first week of July to
the middle of August or thereabout. These plants get mixed up with
grass and are difficult to make out as their capsules appear like grass
blades.

The plants are in dense clusters. The thallus is erect and has a stalk-
like structure at the base and an expanded fan-like part at the apex. The
margin is much dissected. The measurements of the thallus are :—
length 13 mm., breadth at the apex 5 mm. and the thickness at the base
2 mm. The thallus is cavernous and contains a few nostoc colonies. The
surface cells are short and mostly rectangular. They measure 35μ—70μ
$\times 21\mu$—28μ. The plants are monoecious. The antheridial cham-
bers are developed on the dorsal surface. Each chamber contains about
ten antheridia which are stalked. The antheridium is oval in form and
measures 91μ-$98\mu \times 63\mu$-70μ. Each thallus generally bears capsules
from 8 to 10 but this number varies to some extent. The capsules are
up to 30 mm. long with many stomatal structures on them. A stoma
with its guard cells measures $63\mu \times 39\mu$. Involucres are 5 mm. long,
solitary or fused in pairs. The spores are 37μ-40μ in diameter and have
a spiny surface. They are pale in colour. The elaters are large in
number and are jointed. They consist of 3 to 5 cells.

This form does not approach any of the 43 species described by Stephani
with cavernous thallus and pale spores. When compared with the
Indian species it closely resembles *A. erectus*, Kashyap, but the sexuality
and the colour and the surface structure of the spore are important
diagnostic characters in which this form differs from it. (The point of
sexuality, however, is not very material as *A. erectus* is reported to be
monoecious also). Thus it is obvious that the form under consideration
is quite a new one and the author is naming it as *Anthoceros sahyadrensis*
sp. nov. after the name of the Sahyadri mountain on which it is found.

Anthoceros sahyadrensis var. Poona (Pl. II ; Figs. 6)

This form grows on the rocky soil near the Panch Pandav, on the Fer-
gusson College Hill, Poona which is about 1800 feet above the sea level.
(It should however be noted that *Anthoceros Linn.* is by no means in
abundance in Poona. It is restricted only to small areas like the one
described here.) It is usually found during the middle of the rainy
season, *i.e.*, from the last week of July to the end of August after which it
dries up as the conditions grow dry.

The plants are in dense clusters. The thallus is slender, thin, light
green in colour and has a stalk-like structure at the base and an expanded

fan-like part at the apex. The thallus is sub-erect. The margin is
much dissected. The measurements of the thallus are :—Length 5-6 mm.,
breadth at the apex 4-5 mm. and the thickness at the base 2 mm. The
thallus is cavernous and contains a few nostoc colonies The surface
cells of the thallus are polygonal and measure 42μ-$56\mu \times 35\mu$-49μ. The
plants are monoecious. The antheridial chambers are developed on the
dorsal surface. Each chamber has 8-12 antheridia which are stalked.
The antheridium is oval in form and measures $105\mu \times 56\mu$. The
thallus bears 4-5 capsules but the number is varying. The maximum
number of capsules observed was ten. The capsules are about 16 mm.
long with many stomatal structures on them. A stoma with the guard
cells measures $56\mu \times 42\mu$. The involucres are often fused in pairs or
in threes and are up to 2.5 mm. long. The spores are up to 47μ in
diameter and have a spiny surface. The spines are rather blunt. The
spores are pale in colour. The elaters which are few in number are short
and jointed and consist of two to four cells.

A comparison of this form with the 43 species of Anthoceros with
cavernous thallus and pale spores shows that it approaches *Anthoceros
bulbiferous St.* but the latter being dioecious is out of consideration. Again
when this form is compared with the Indian species so far described it is
found that it resembles *A. Longii St.*   But *A. Longii St.* differs from the
present form in having solitary involucres and black spores which are
important diagnostic characters. When compared with *A. sahyadrensis*
sp. nov. which is described above, it is seen that it differs in the structure
and size of the surface cells of the thallus and in the lengths of the invo-
lucre and the capsule, but it closely agrees with it in the general appear-
ance of the plant body, and colour and structure of the spore. These
considerations make the author look upon this form provisionally as a
variety of *A. sahyadrensis* and he names it as '*A. sahyadrensis var. Poona.*'

Anthoceros sahyadrensis var. Purandhar (Pl. III; Figs. 7)

This form was collected from Purandhar hill which is about 4472 feet
high from the sea-level. The plants are in clusters. The thallus is erect,
fan-shaped and bluish green in colour. The margin of the thallus is much
dissected. The thallus is 8-10 mm. long and is 4-8 mm broad at the
apex. The base of the stalk is about 2 mm. thick. The thallus is caver-
nous and contains large nostoc colonies. The surface cells are mostly
elongated rectangles and measure 49μ-$84\mu \times 21\mu$-28μ. The plants are
monoecious. Antheridial chambers are few in number and are developed
on the dorsal surface. Each chamber contains 5-10 antheridia which
are stalked. The antheridium is oval in form and measures $91\mu \times 70\mu$.
The stalk is about 91μ long. Involcures are 4.5 mm. long, solitary or
fused in pairs. The capsules are up to 18 mm. long with stomatal struc-
tures on them. Each stomatal aperture with its two guard cells is about
42μ-$49\mu \times 56\mu$-63μ. The spores are 40μ in diameter and have a spiny
surface. The spines are rather blunt. The colour of the spore is pale.

A comparison of this form with the Indian species so far described
and the 43 species described by Stephani with cavernous thallus and pale
spores shows that this form comes very near to *A. erectus* Kash. and *A.
Butleri St.* But *A. erectus* has black spores and longer capsules and hence
needs no further consideration. *A. Butleri St.* has solitary involucres and

only two antheridia in each chamber while the form under consideration has solitary as well as fused involucres and many antheridia in each chamber. When compared with *A. sahyadrensis* described ·above it differs in the colour of the thallus, the length of the capsule and in the size and shape of the surface cells of the thallus ; but it very closely ·agrees with the general form of the plant body and the colour and structure of the spore which are important characters and hence it is thought better to call provisionally this form as a variety of *A. sahyadrensis* and the author is naming it as '*A. sahyadrensis var. Purandhar*'.

Anthoceros Dixiti sp. nov. (Pl. IV; Figs. 11)

This form is found growing on the black stones of a compound wall at Lonavla towards the end of the rainy season in the third week of September.

The plants are dioecious and grow in large patches very close to the surface of the black stone. Each plant is a rosette and is dichotomously branched with the segments slightly overlapping along the margin. The segments are 20 to 25 mm. long and 3 to 5.5 mm. broad. The margin is wavy or toothed. The thallus is solid and greenish yellow in colour. The surface cells are polygonal and have practically the same length and breadth. They measure 21μ-$28\mu \times 28\mu$-35μ. Frcm the ventral side small tubers are given out.

The male plants when growing singly are circular in form and branch dichotomously. Each segment is about 10 mm. long and from 3 to 4 mm. broad. The antheridial chambers are borne on the dorsal side, generally along the median line. Each antheridial chamber contains only four antheridia. The antheridium is very large and practically spherical. Its dimensions are 161μ-$196\mu \times 196\mu$-210μ. The stalk of the antheridium is very short and measures 77μ.

The female plants when occurring singly are much larger than the similar male plants and are circular in shape. Capsules are developed on the dorsal side and are generally very few, 2 or 3, on each lobe of the thallus. They are robust in appearance and are up to 16 mm. long. Stomatal structures are present on the wall of the capsule. Each stoma with its two guard cells measures $77\mu \times 56\mu$. The involucre is up to 4 mm. long. The spores are 40μ in diameter and have a spiny surface. The spines are very small. The colour of the spores is bright yellow. The elaters are short, bent and jointed, and consist of 2 to 3 cells each.

The solid thallus and the golden yellow spores have made the identification of this form rather easy. Of the Indian species there are only two species with yellow spores and solid thalli—*A. himalayensis* Kash. and *A. Jackii* St. *A. Jackii* St. is monoecious and hence is out of consideration. A comparison of this form with the type specimens of *Anthoceros himalayensis* Kash., which were secured from Lahore, shows that differences in the following points are self-evident :—The length of the capsule and the size of the spore. This form also does not agree with any of the species given in the table by Khanna describing Anthoceros species with solid thallus and pale spores. It is clear therefore, that this form is quite a new species and hence is named after the author's revered teacher Professor D. L. Dixit as '*Anthoceros Dixiti* sp. nov'.

Unidentified forms of Anthoceros with yellow spores.

Anthoceros specimen No. I (Pl. V, Fig. 1)

Thallus yellowish green and thin. Margin not crisped. Largest thallus about 10 mm. in length. Involucre 4.5 mm. Capsule up to 30 mm. Spores 35μ to 38μ, yellow. Locality—Mahabaleshwar. 4500 feet above the sea-level.

Anthoceros Specimen No. II (Pl. V, Figs. 2, 3)

Thallus small. Involucre 3 to 3.5 mm. Capsules 35 mm.; rarely up to 50 mm. Spores 34μ, yellow.

Locality—Mahabaleshwar. 4500 feet above the sea-level.

Anthoceros Specimen No. III (Pl. V, Fig. 4)

Thallus small. Involucre 3.5 to 4 mm. Capsule 45 mm. Spores yellow, up to 34μ.

Locality—Bheemashankar. 3400 feet above the sea-level.

It seems that specimen No. I is identical with *A. Jackii* St. The only difference is in the length of the involucre. Specimen Nos. II and III appear to be identical and are from two localities. These specimens do not agree with any of the yellow spored species so far described from India.

NOTE

These three forms of Anthoceros with yellow spores (Specimen Nos. I, II, III) are from places about 4500 feet high. The plants present quite a different physiognomy, although the length of the involucre, the length of the capsule, the colour, size and surface structure of the spore are practically the same in all the three forms. It is difficult to say whether they all belong to the same species showing differences due to the environment or whether they belong to different species. Further work is in progress.

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EXPLANATION OF PLATES

PLATE I

ANTHOCEROS SAHYADRENSIS, SP. NOV.

Figs.—1. Plant with sporogonia; 2. Surface cells from the dorsal side of the thallus; 3. T. S. of the thallus—only in part; 4. T. S. of the involucre—only in part; 5. Stoma from the capsule; 6. Spore with elaters; 7. Bunch of antheridia—only in part.

PLATE II

ANTHOCEROS SAHYADRENSIS, VAR. POONA

Figs.—1. Plant with sporogonia; 2. T. S. of the thallus and the involucre, 3. Surface cells from the dorsal side of the thallus; 4. Stoma from the capsule; 5. Spore with elaters; 6. Bunch of spent up antheridia.

PLATE III

ANTHOCEROS SAHYADRENSIS, VAR. PURANDHAR

Figs.—1. Plant with sporogonia; 2. T. S. of the thallus—only in part; 3. T. S. of the involucre—only in part; 4. Stoma from the capsule; 5. Surface cells from the dorsal side of the thallus; 6. Spore with elaters; 7. Bunch of spent up antheridia—only in part.

PLATE IV

ANTHOCEROS DIXITI, SP. NOV.

Figs.—1. Female plant with sporogonia, 2. A segment of the female plant with sporogonia; 3. Male plant; 4. Ventral view of a segment of the thallus showing tubers; 5. Segment of the male plant showing antheridial chambers; 6. T. S. of the thallus—only in part; 7. Surface cells from the dorsal side of the thallus; 8. Stoma from the capsule; 9. T. S. of the involucre—only in part; 10. Spore and elaters; 11. Bunch of antheridia.

PLATE V

UNIDENTIFIED FORMS OF ANTHOCEROS WITH YELLOW SPORES

Figs.—1. Plant with sporogonia, speciment No. I, Mahableshwar; 2 and 3. Plants with sporogonia, specimen No. II, Mahableshwar; 4. Plant with sporogonia, specimen No. III, Bheemashankar.

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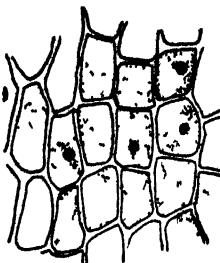
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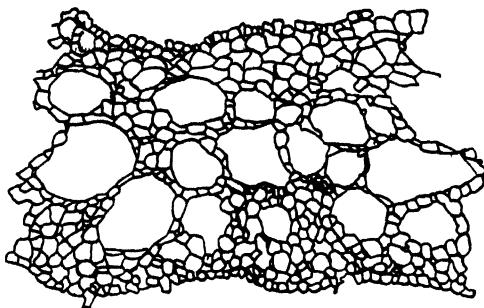
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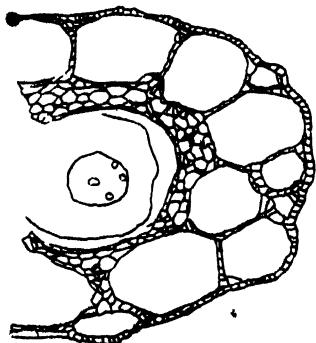
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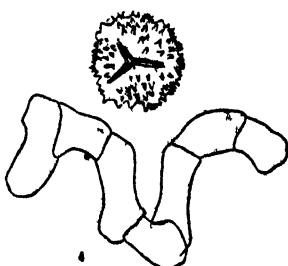
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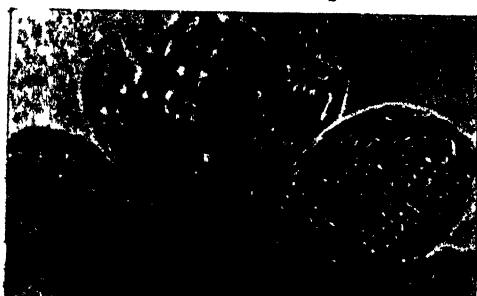
Fig. 7 ×400

PLATE II

Fig. 1 ×3
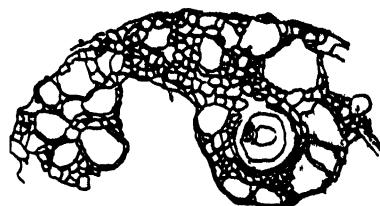
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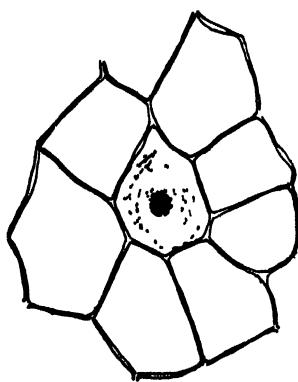
Fig. 3 ×360
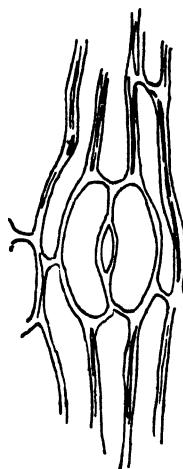
Fig. 4 ×360
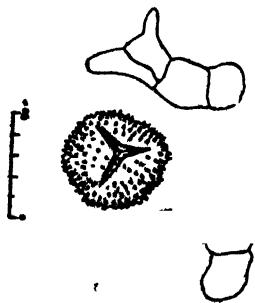
Fig. 5

Fig. 6

PLATE III
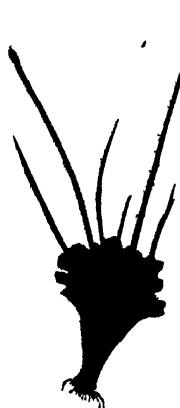
Fig. 1 ×2
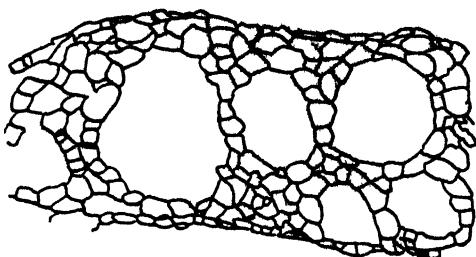
Fig 2 ×81
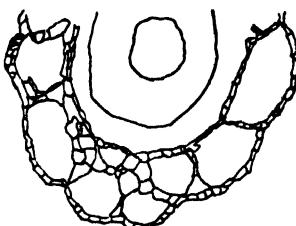
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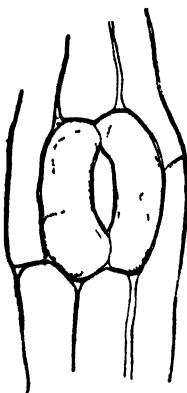
Fig. 4 ×360
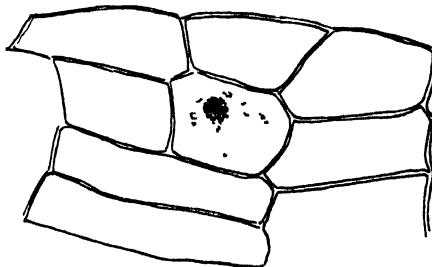
Fig 5 ×360

Fig. 6 ×250
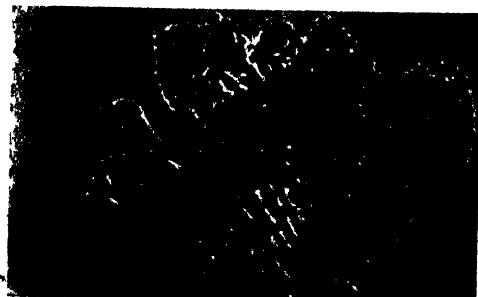
Fig. 7 ×230

PLATE IV

Fig. 1 ×¾
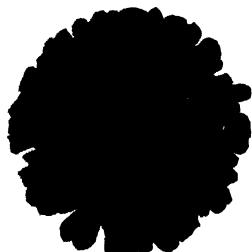
Fig. 2 ×1½
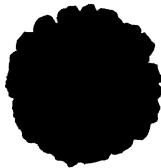
Fig. 3 ×1

Fig. 4

Fig. 5 ×2
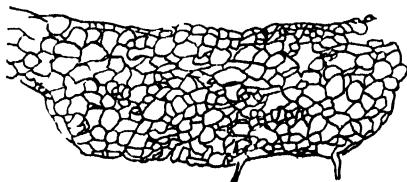
F.g. 6 ×33

Fig. 7 ×145
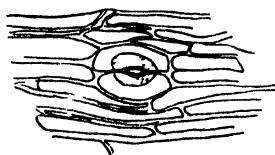
Fig. 8 ×145
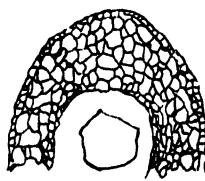
Fig. 9 ×33
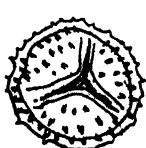
Fig. 10 ×500

Fig. 11 ×90

PLATE V

Fig. 1 ×4
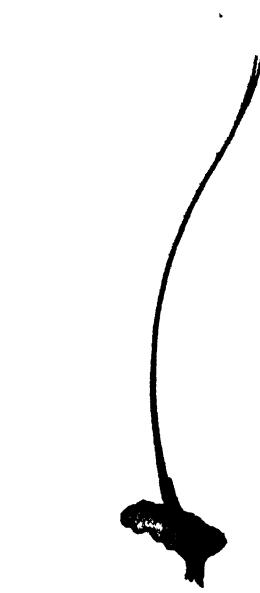
Fig. 3 ×$\frac{4}{5}$

Fig. 2 ×$\frac{4}{5}$
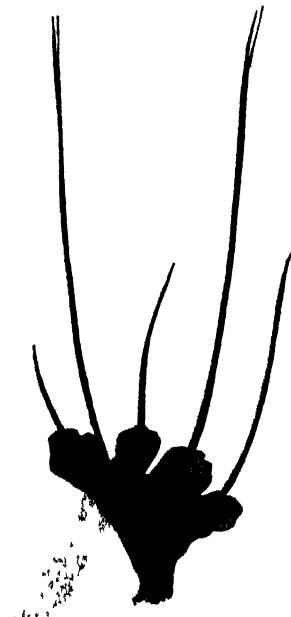
Fig. 4 ×1$\frac{1}{2}$

STUDIES IN THE ECOLOGY OF MANGROVES

III. The Chloride-content of Sea-water, Soil-solution and the Leaf Cell-sap of the Mangroves

By

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AND

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INTRODUCTION

THE chloride-content (chiefly of NaCl) of the sea-water, soil-solution and the leaf cell-sap plays an important part in the growth of the mangrove vegetation. As the sea-water contains a rather large percentage of NaCl, the vegetation growing near or in salt marshes does naturally possess a very large amount of this salt, which influences the soil-solution and through it, the cell-sap. Due to it the osmotic pressure of the cell-sap varies.

Recently Walter and his co-workers (11-16) in their studies on the East African mangroves have shown that the different zones formed in this type of vegetation are largely due to the capacity of the plants to bear increasing or decreasing amounts of chloride of the soil. Thus they distinguish several zones as those of Sonneratia, Rhizophora, Ceriops, Avicennia, etc. Those of Avicennia and Rhizophora, for example, can bear greater fluctuations in the chloride-content than Sonneratia which requires a constant chloride-content. The osmotic value due to the chloride-content of the cell-sap is represented as the percentage of the total osmotic value of the entire cell-sap.

Not only the zonation depends upon the chloride-content of the soil but also the morphological and anatomical differences, for exmaple, the succulence of the leaves.

Thus the above studies and those of Adriani (1), Chapman (2, 3, 4), Cooper and Pasha (5, 6), Drabble and Lake (7), Harris and Lawrence (8), Hill (9), Maximov (10) and Steiner (11) have conclusively shown the great rôle of the salt-content of the sea-water and of the soil in the

bionomics of the mangrove vegetation.   In spite of the recognition of this important fact, it is found that no regular observations spread over a year or more have so far been made by any worker.   To fill this gap and to find out whether any other new factors are involved in it the present study was pursued.

METHOD

The chloride-content was determined by the volumetric method of titrating the sample against a known standard silver nitrate solution.

The samples of the leaves of Avicennia alba Bl. from the Colaba Reclamation and the Vadala salt pan regions were collected in special unbreakable glass tubes with corks, fitted in air-tight aluminium boxes. For this purpose only normal healthy leaves were chosen.   After bringing them to the laboratory, the boxes were put in boiling water for 20 minutes (12).   This was done with a view to killing the plant material as quickly as possible in order to prevent any alterations taking place in the tissues.   A suitable method, according to Walter, of killing the plant material is to heat the tissue to 100° C which destroys the enzymes and partially sterilises the tissues.

In the present case the heating was done in a boiling water-bath in which the aluminium boxes were placed erect.   After cooling, the cell-sap was extracted from the leaves by means of a silver-plated brass-extractor and was collected in special hard-glass test tubes.

As the cell-sap was distinctly acidic and dirty-green in colour, potassium chromate as indicator could not be used directly.   Therefore, the sap was first treated with calcium carbonate to neutralize its acidic nature and then the indicator added.   For this a saturated solution of pure calcium carbonate was used and then titrated with the silver nitrate solution of the strength of 1 c.c. equal to 1 mgm. of chlorine.   Three readings were always taken for one sample and their mean was recorded as the final reading.

As regards the sea-water samples, they were brought to the laboratory in bottles with well-fitting corks.   Before filling, the bottles were washed with sea-water twice or thrice.   After bringing the samples to the laboratory, they were kept undisturbed for 75 hours in order to allow all the suspended matter to settle down.   For titration a few c.c. were taken out by means of a pipette without disturbing the sediment at the bottom.

Soil-solutions were prepared by taking 40 gms. of soil in 100 c. c. of distilled water and kept over night after shaking for an hour in a shaker. From the bottles in which these solutions were kept 1 c.c. of the supernatent liquid was taken and titrated against the standard silver nitrate solution.   From the latter, chlorine in terms of sodium chloride per 100 parts of the extracted solution was calculated.

RESULTS AND DISCUSSION

Tables I and II give the chloride-content in terms of sodium chloride of the sea-water, the soil-solution and the leaf cell-sap of Avicennia alba.

TABLE I

CHLORIDE-CONTENT IN TERMS OF SODIUM CHLORIDE OF COLABA SAMPLES
(MONTHLY SERIES)

Date	In 100 c.c. of Sea-water	In 100 c.c. of Soil-solution	In 100 c.c. of Leaf Cell-sap	Season
9-9-36	2.31	0.40	...	
30-9-36	3.77	1.04	....	Rainy
14-10-36	3.49	1.17	....	
30-10-36	3.43	1.20	. ..	
21-11-36	3.35	1.13	....	Cold
18-12-36	3.08	1.43	....	
29-1-37	3 41	0.81	...	
27-2-37	3.74	1.54	2.80	
22-3-37	3.58	1.40	3.52	
22-4-37	3.64	1.20	3.56	Hot
18-5-37	3.66	1.40	4.03	
18-6-37	3.20	1.25	2.91	
15-7-37	2.06	0.47	2.60	
23-8-37	2.37	0.94	3.61	Rainy
29-9-37	0.77	0.35	2.45	
7-10-37	3.35	1.46	2.89	
19-11-37	3.61	2.06	3.76	Cold
8-12-37	3.47	1.31	4 97	

The above Table I indicates that the samples of leaves were collected from February 1937 to January 1938.

It will be apparent from Table I and Fig. 1 that the chloride-content of the leaf cell-sap of Avicennia alba varies from 2.60 to 4.97. For the same period the fluctuations in the chloride-content of the sea-water is from 0.77 to 3.74, whereas that of the soil-solution varies from 0.40 to 2.06. However, it must be pointed out here that in spite of the differences the three curves representing leaf cell-sap, soil-solution and sea-water run parallel to each other throughout the year. The chloride values remain almost constant for the first 4 months of the year and then begin to fall reaching the minimum in September. From this month the chloride-content increases and attains its maximum in December. From this it seems that the fluctuations in the chloride-content are influenced by the seasons and that they fall down during rains and rise in the other seasons. That this is true can be seen from Fig. 2, where it will be found that the chloride-content falls when there is rain and rises when it stops.

This phenomenon can be observed even during the monsoon if there happens to be a dry spell of weather. For example, on 23rd August, i.e., during the monsoon of 1937 when the rain had stopped, the chloride-content showed an abrupt rise. It will also be observed that not only the chlorides had increased in the cell-sap but had also risen in the sea-water, as can be seen from Fig. 1.

On the other hand on 23rd September 1937 there is a sudden marked fall in the value of the chloride-content of both the cell-sap and sea-water,

CHLORIDE IN TERMS OF NaCl PER 100 PARTS.

LEAF CELL SAP
SEA WATER
SOIL (H₂O EXTRACT)
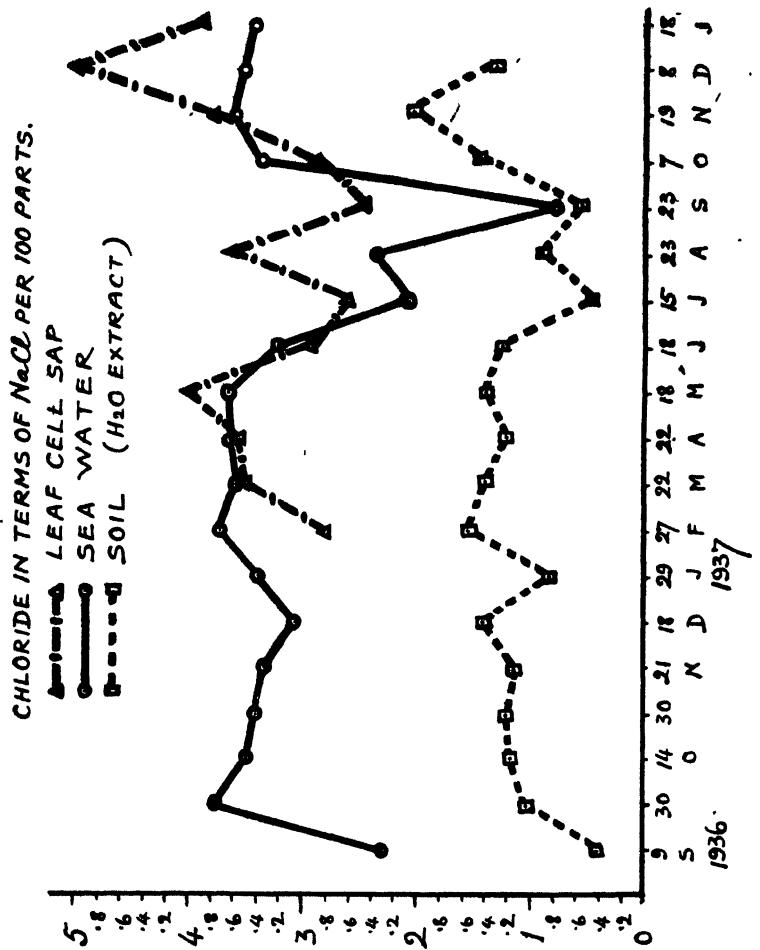
Fig. 1
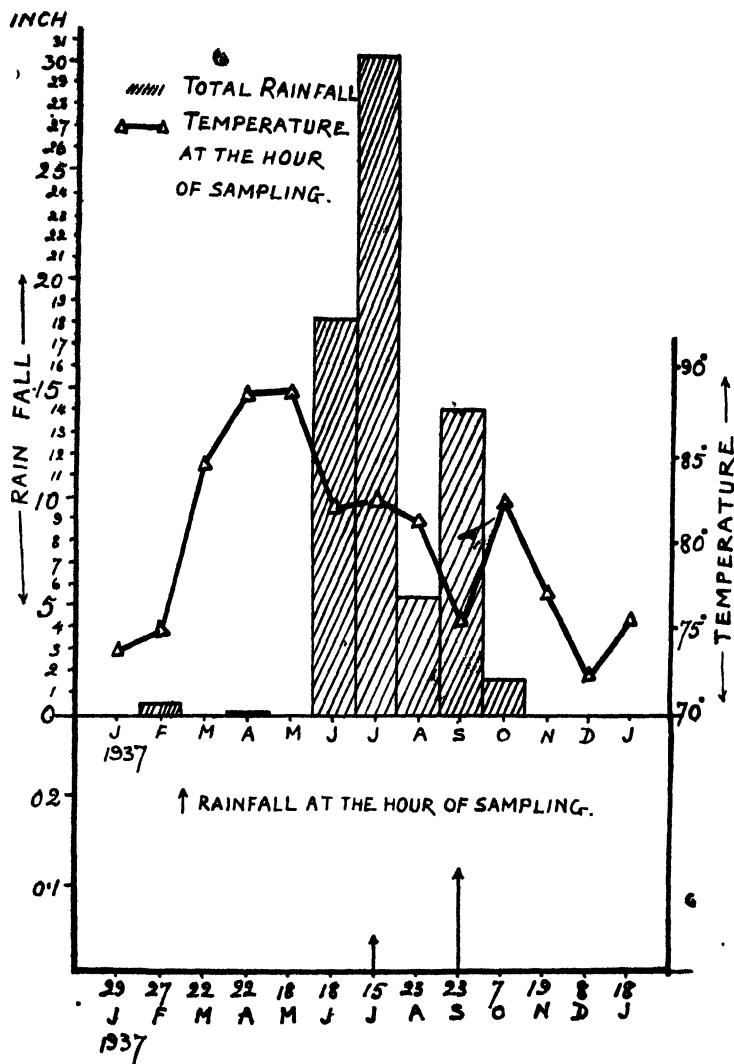
Fig. 2

as there was a heavy downpour of rain throughout the previous night and the samples were collected early in the morning at 7.40 a.m. Hence the direct effect of rainfall in lowering the chloride-content is obvious.

Another series of collection of weekly samples was carried out from the 5th August 1939 to the 29th February 1940 (vide Table II).

TABLE II

CHLORIDE-CONTENT IN TERMS OF SODIUM CHLORIDE OF COLABA SAMPLES (WEEKLY SERIES)

Date	In 100 c.c. of Sea-water	In 100 c.c. of Soil-solution	In 100 c.c. of Leaf Cell-sap	Season
5- 8-39	2.49	1.28	3.03	
12- 8-39	2.83	1.34	3.04	
19- 8-39	3.26	1.56	2.82	
2- 9-39	1.51	0.78	1.99	
9- 9-39	2.03	0.86	2.00	Rainy
15- 9-39	2.22	1.31	1.85	
23- 9-39	2.83	1.08	1.86	
30- 9-39	0.91	1.61	1.59	
6-10-39	3.24	1.65	2.88	
13-10-39	3.17	1.84	3.11	
20-10-39	3.50	2.69	2.36	
26-10-39	3.51	1.27	3.40	
2-11-39	3.53	2.52	4.40	
8-11-39	3.45	1.72	3.59	
17-11-39	3.46	2.54	4.34	Cold
23-11-39	3.50	2.20	4.79	
30-11-39	3.45	2.88	4.64	
7-12-39	3.49	1.51	3.97	
14-12-39	3.53	2.87	4.88	
21-12-39	3.59	2.68	4.52	
28-12-39	3.48	3.39	4.17	
4- 1-40	3.51	2.60	5 05	
11- 1-40	3.47	3.47	3.68	
18- 1-40	3.46	3.29	2.31	
22- 1-40	3.39	2.57	3.73	
25- 1-40	3.47	3.11	3.60	
1- 2-40	3.50	3.31	5.05	
8- 2-40	3.43	2.98	3.55	
15- 2-40	3.45	3.08	4.46	Hot
22- 2-40	3.48	3.39	3.69	
29- 2-40	3.47	3.34	5.03	

From this series it is apparent that the chloride-content of the leaf cell-sap varies from 1.59 to 5.05; that of the sea-water from 0.91 to 3.59 and that of the soil-solution from 0.78 to 3.47. These results agree with those of the monthly series. But a remarkable fact to be noticed in the case of the sea-water is that the fluctuation in its chloride-content is very small from the 6th October 1939 to the 29th February 1940.

The results of the above weekly series support the statement already made that the rainfall and temperature are the immediate causes of the fluctuation in the chloride-content.

Comparing the values of the chloride of the cell-sap during the monsoon and the other seasons, it is found that it is less during rains. To account for this, Cooper and Pasha (5 and 6) have suggested that "during the monsoon the transpiratory activity will be lessened and the plants will absorb more water than is lost by transpiration and consequently the osmotic pressure of the plant organs will be lowered." But this explanation is based on irregularly collected and insufficient data. The osmotic pressure of the cell-sap of the leaf can decrease during the monsoon due either to (1) dilution of the soil water or (2) greater absorption of water during the monsoon, as suggested by the above authors. In support of the latter hypothesis they have not produced any experimental evidence to show that during the monsoon the cells actually contain more water than in the other seasons. Nor have they shown that the higher water-content of the cells in the monsoon is sufficient to account for the observed lower osmotic pressure and the consequent lower chloride-content. Hence in the light of the present data the former explanation that the chloride-content of the cell-sap in the monsoon falls due to the dilution of the soil- and sea-water seems to be correct. This can be seen from Fig. 1 which shows how the three curves of the chlorides of the cell-sap, soil-solution and sea-water run parallel to each other.

EFFECT OF TIDES ON THE CHLORIDE-CONTENT

The tides seem to have an effect on the concentrations of the sea-water, the soil-solution and the leaf cell-sap. The low tide tends to increase the concentration of chlorides. Due to evaporation salts are deposited near the shore. This causes a high concentration of the sea-water and when the sea-water is thus affected, it naturally influences the soil-solution and by the concentrated soil-solution, the cell-sap is found to increase in its chloride-content.

Similarly at the high tide, the reverse of the above process takes place. Firstly the sea-water gets less concentrated due to dilution of water at high tide and its effect is seen on the cell-sap through the soil-solution getting weak in concentration.
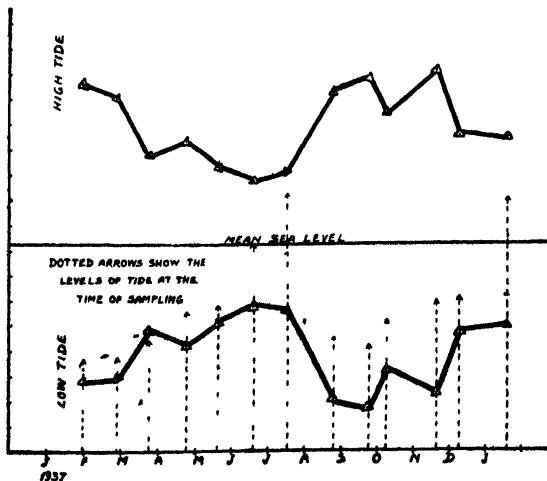

Fig. 3

Those remarks are not only noticed from the Tables I and II and the graph of the chloride-content (Fig. 1) and the corresponding tide graphs (Fig. 3) but from special experiments carried out to note the effect of tides on the chloride-content.   In these experiments the read-ings of the low and high tides were taken on the same day, so that it is easier here to compare the results than from the monthly or weekly readings.   The results obtained are tabulated in the following table.

TABLE III

	Chloride-content in 100 c.c.	
	High tide	Low tide
1. Sea-water	3.43	3.54
2. Sea-water	3.38	3.39
1. Soil-solution	2.57	2.69
2. Soil -solution	2.83	3.16
1. Cell-sap	4.60	4.72
2. Cell-sup	3.51	3.72

The above figures distinctly show that the concentration of the sea-water, the soil-solution and the cell-sap is higher at low tide and vice versa. This is further confirmed by the following results obtained by Walter on the osmotic pressure of the soil-solution.

TABLE IV

Low Tide	32 6 atms.
High Tide	32 3 ,,

DIFFERENCE BETWEEN ADULT AND YOUNG LEAVES

Though there are but a few observations to record on the difference in the chloride-content of adult and young leaves yet they are worth noting here. The five observations which are noted in Table V show that in the chloride-content the young leaves show lower values than the adult. This is not surprising for the young leaves have lower salt-content. For the above reason and due to the fact that the young leaves are not available throughout the year, it was best to take the adult leaves for the determination of the osmotic pressure and the chloride-content.

TABLE V

Date	Chloride-content in 100 c.c. of Adult Leaf Cell-sap	Chloride-content in 100 c.c. of Young Leaf Cell-sap
13-10-39	3.11	3.07
26-10-39	3.40	2.39
2-11-39	4.40	3.06
9-11-39	3.59	3.27
17-11-39	4.34	3.87

COMPARISON OF THE CHLORIDE-CONTENT OF THE CELL-SAP OF AVICENNIA
ALBA WITH THAT OF OTHER MANGROVES

Though much data is not accumulated on this interesting point, a few observations made on other species of mangroves (vide Table VI) are worth noticing.

TABLE VI

CHLORIDE-CONTENT IN 100 C.C.

Date	Locality	Name of Plant	Cell-sap
7-2-37	Vadala	Sesuvium Portulacastrum	2.00
13-2-37	,,	,, ,,	3.47
21-5-39	Mumbra Diva Creek	Sonneratia apetala	2.81
21-5-39	,, ,,	Acanthus ilicifolius	2.37
25-5-39	Mahim Bandra Creek	Rhizophora mucronata	2.52
25-5-39	,, ,,	Bruguiera gymnorhiza	2.68
25-5-39	,, ,,	Ceriops candolleana	2.53

From the above Table it will be seen that the cell-sap of Avicennia alba seems to contain a higher percentage of chloride than any other of the mangrove species. Perhaps it is this peculiarity which allows it to grow where other mangrove plants are not able to thrive and which makes it the dominant plant of the foreshore of the Bombay and Salsette Islands. The shores of Bombay and Salsette Islands being generally rocky do not extend far inland (except at places like Ghodbunder) and therefore it is rarely that any other plant except Avicennia alba is found on these shores.

CONCLUSION

(1) The chloride-content of the sea-water and that of the soil-solution are influenced by rainfall and temperature. This can be seen from the fact that during the monsoon it falls, and it rises during summer and the cold season.

(2) Similarly the rainfall and the temperature affect the chloride-content of the cell-sap.

(3) Hence the seasonal variations in the chloride-content of the leaf-cell-sap are directly dependent upon the climatic conditions and not as Cooper and Pasha (5,6) have maintained, primarily upon the physiological conditions. This is also supported by previous experiments of Hill (9).

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SHRINKAGE IN PLAICE EGGS

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THE pelagic fish eggs are generally identified with the help of their size, shape, presence or absence of oil globule or globules, nature of the yolk and the egg capsule, and such other distinguishing features. However the final determination of the majority of them depends to a great extent upon their size. But the eggs may be collected in large numbers, often under conditions which make it impossible for all of them to be identified in the living state ; consequently they have to be fixed for examination sometime later.

Under such circumstances it is useful to have an idea of the decrease in size due to preservatives among which formalin is the most commonly used fluid. Such an estimation of decrease will be particularly useful in the identification of some preserved eggs of fishes (*e.g.*, Pleuronectids, Gadoids, etc.), as the eggs of some species are not only alike in appearance but also have overlapping dimensions.

Accordingly as a preliminary study fifty eggs of the plaice (P. platessa) were measured across the diameter while living and then fixed in 5% formalin in sea water. They were measured again after five months immersion in formalin and all showed a certain amount of reduction in size. The shrinkage, as seen from the following figures, varies from 0.04 to 0.08 m.m. and thus the average loss of diameter per egg is about 0.054 m.m.

This amount of shrinkage, though small as observed by Ehrenbaum[1], is certainly worthy of notice in deciding some border line cases. The author, during his study of fish eggs, and fish larvae of the Manx waters at Port Erin Marine Biological Station found this knowledge of special value in differentiating from the same samples certain small plaice eggs from large cod (G. callarias) eggs, as the minimum diameter of plaice eggs is almost the same as the maximum diameter of cod eggs.[2]

It will therefore be seen that this loss in diameter in preserved eggs, if not taken into consideration, is likely to mislead the identification of certain border line cases and hence it should be studied where possible.

No. of Egg	Diameter in m.m. before fixation	Diameter in m.m. after fixation	Shrinkage in m.m.
1	1.96	1.92	0.04
2	1.90	1.86	0.04
3	2.04	1.98	0.06
4	1.96	1.92	0.04
5	1.90	1.84	0.06
6	1.98	1.92	0.06
7	2.08	2.02	0.06
8	2.00	1.94	0.06
9	2.02	1.94	0.08
10	1.94	1.88	0.06
11	2.14	2.08	0.06
12	2.02	1.96	0.06
13	2.04	1.98	0.06
14	1.92	1.88	0.04
15	2.04	1.98	0.06
16	2.04	1.98	0.06
17	2.00	1.94	0.06
18	2.00	1.94	0.06
19	1.98	1.94	0.04
20	1.88	1.84	0.04
21	2.08	2.02	0.06
22	1.90	1.84	0.06
23	1 94	1.90	0.04
24	2.00	1.92	0.08
25	2.00	1.94	0.06
26	2.08	2.04	0.04
27	2.00	1.96	0.04
28	2.04	1.98	0.06
29	1.88	1.82	0.06
30	1.88	1.84	0.04
31	2.00	1.96	0.04
32	1.96	1.90	0.06
33	2.08	2.00	0.08
34	2.02	1.98	0.04
35	2.04	1.98	0.06
36	2.00	1.94	0.06
37	2.10	2.04	0.06
38	1.96	1.92	0.04
39	2.00	1.96	0.04
40	1.96	1.90	0.06
41	2.02	1.98	0.04
42	1.96	1.92	0.04
43	1.96	1.90	0.06
44	1.98	1.92	0.06
45	1.98	1.92	0.06
46	2.06	2 00	0.06
47	1.90	1.86	0.04
48	2.00	1.96	0.04
49	2.08	2.02	0.06
50	1.90	1.84	0.06

A similar number of eggs of plaice was measured and fixed in 5% formalin in fresh water and the shrinkage was found to be of the same order.

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